eters are non-random (without being special); without separate consideration of different classes of intensities, misleading trial models may be found.

ABRAHAMS: This particular structure (based on space group *Pba*2) does not closely approximate a higher symmetry space group.

ALEXANDER: (*a*) We have noted the tendency to apply factors of the order of 1·5 to 2·0 to conventional *R* values to soak up the inaccuracies that we realize to be present, but still the figures do not put us on a correct statistical basis.

(*b*) The χ^2 distribution method for the detection of systematic error may have a parallel with the work of the late Mr K. Beu on the determination of precise lattice parameters.

LADELL: Would you consider chemical structural results as allowable as an internal check, *e.g.* the coplanarity of five particular atoms in a structure?

ABRAHAMS: I suppose it is permissible to refer to internal consistency in respect of chemical features, provided this is specifically stated; *e.g.* if there are two molecules in the asymmetric unit, conclusions may be derived on the assumption that these are in fact identical. However, the experimental accuracy of the measured *F* cannot easily be assessed quantitatively in this way.

RIVA DI SANSEVERINO: Concerning your criticism of the use of unit weights, when do you consider that a statistically acceptable weighting scheme should be used?

ABRAHAMS: I would consider it correct to use the estimated weights, as outlined above, at all stages.

HAMILTON: In the early stages of analysis while one is still trying to solve the structure, or before one has reached the linear range of least squares, perhaps one may choose to use artificial weighting schemes to reject or down-weight weak or strong terms or modify terms in a selected angular range.

RIVA DI SANSEVERINO: In your alteration of the weighting scheme, you may be adjusting the situation to what you expect or desire.

SANDOR: The study of the effect of simulated systematic errors on a hypothetical structure shows hardly any correlation between the errors in the positional and thermal parameters of the atoms. I wonder how far this apparent lack of correlation applies to real cases where various types of systematic and random errors occur simultaneously.

Would it not be worth extending the present study by mixing various types of errors and study their combined effect on the errors of the positional and thermal parameters of a hypothetical structure?

ABRAHAMS: We plan to do this.

Real Crystals as a Source of Error

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Specimen-dependent properties of real crystals which influence the accuracy of intensity measurement are size, shape, homogeneity, stability and environment. Variations of any of these will affect the corrections necessary to allow for absorption and extinction in a given experimental measurement; these in turn will affect the evaluation of the absolute intensity, and the two principal tests for internal and external consistency, namely variation within any form $\{hkl\}$, and variation of mean values $I\{hkl\}$ between different specimens. They may also affect the relative values of $I\{hkl\}$ within one data set, leading for example to spurious anharmonicity in the temperature factors derived for an ellipsoidal crystal. Examples of practical solutions of actual problems involve waxes instead of glues for crystal mounting, miniature films or intensifying screens for use in unstable situations or with very small crystals, integrated oscillation photographs for intensity measurements from poor specimens, rotation photographs for high symmetry crystals, the use of Laue photographs for the detection of order-disorder phenomena, and the incorporation of an iron-55 source in an automated diffractometer to provide an internal standard for intensity measurements.

Introduction

The influence of specimen-dependent properties of real crystals on the accuracy with which the intensities can be measured may be summarized in the diagram in Fig. 1. The existence of these effects has been known for many years, and the purpose of this paper is to focus attention on the fact that because many of these problems often confront the average experimenter

simultaneously, the precision attainable in individual counter measurements (better than 1 %) can seldom be utilized to achieve structure amplitudes of comparable accuracy. Even the precision of individual photographic intensity measurements, at best about 2 %, cannot generally be transferred to the final list of $F(hkl)$.

The fundamental problem, therefore, consists firstly in recognizing what type of errors introduced by the nature of the specimen will seriously affect the type of

information being sought, and secondly in measuring or at least estimating these errors, since it is unrealistic to assume that they can be completely eliminated. Particular errors can, however, sometimes be circumvented to a considerable extent by adopting non-standard procedures, or by making minor modifications to standard equipment, and this implies that a rather flexible approach to individual problems may be more efficient than the routine collection of all available data by a standardized procedure, however admirable it may seem.

One real advantage of fast computers which crystallographers in general seem to have been very slow to exploit, is the possibility of making detailled calculations *in advance* to decide upon which reflexions they should concentrate in order to solve specific problems. This may be illustrated by one of the uncertainties most frequently encountered in practice, namely the difficulty of establishing the presence or absence of a centre of symmetry. In the structure of chromium hexacarbonyl (Whitaker & Jeffery 1967), which may be assigned to $Pn2_1a$ or $Pnma$, the Cr atom is either on or near the plane at $y=\frac{1}{4}$, and hence this is not a favourable case for making a decision from the inequality of reflexions $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$ for the data set as a whole due to anomalous dispersion. However, for Cu $K\alpha$ radiation, which was used, $\Delta f'=-0\cdot1$ and $\Delta f''=2\cdot6$ for Cr, whereas for Cr $K\alpha$ radiation, $\Delta f'=-2\cdot2$ and $\Delta f''=0\cdot7$ (*International Tables for X-ray Crystallography*, 1962, Vol III, 'p.213). The modulus of the complex scattering factor was in fact used in the calculations, but now that the structure is known, it might be possible to find one or more *particular* reflexions which could decide the question, or at least set an upper limit on the deviation from centro-symmetry.

The first difficulty often encountered with real crystals is purely geometrical; the crystal may be singly or multiply twinned. Twinning is not generally a serious problem where it can be recognized easily; but when appreciable numbers of reflexions from the different individuals are superposed, it can be. This is too wide a subject to discuss here, but non-crystallographers who manage to obtain a few quick X-ray pictures of a crystal to use in conjunction with other types of physical or chemical measurements do not always recognize the presence of twinning, and they should be especially suspicious if their results seem a bit peculiar in the given context.

(a) Crystal size (especially small crystals)

When only very small crystals are available, the time taken for data collection becomes prohibitive, even when the crystals are stable. In addition, if the reflexions do not rise high enough above the background, the intensities are likely to be rather inaccurate. We have been experimenting with two methods of dealing with this problem, namely miniature films and intensifying screens.

The case for miniature films rests mainly on the inverse square law. A film of 1 cm radius should require only $\frac{1}{9}$ of the exposure of a 3 cm radius film. In fact the situation is not quite as favourable as this, because the beam diverges from a crystal of finite size, not from a point, but it is still a large factor. Miniature films have been tried in the past, but the method did not become popular owing to the difficulty of measuring the intensities. However, now that large magnifications can be obtained with the Isodensitracer (Fig. 2) miniature films present no greater difficulties than the more usual sizes.

There is no basic reason why small specimen-to-detector distances should not also be used on diffractometers but rather different considerations apply, and indeed *increased* specimen-to-detector distances are sometimes advantageous in increasing the signal-to-background ratio, as they may also be in photographic methods under certain circumstances.

The possibility of using intensifying screens, discounted many years ago on account of real or apparent failure of the reciprocity law, has been brought to our attention by the recent introduction of Polaroid cameras for X-ray and neutron diffraction studies [see for example Smith & Holcomb (1963)]. These
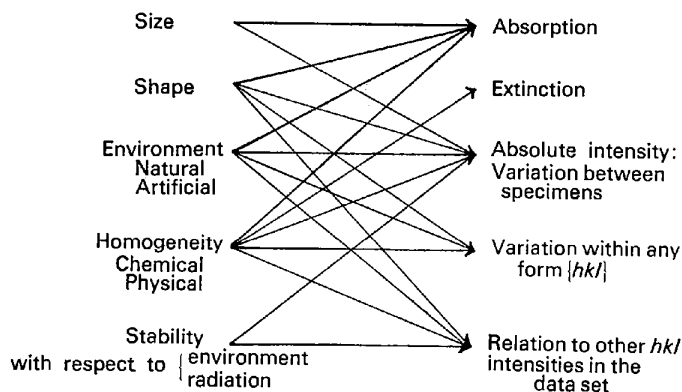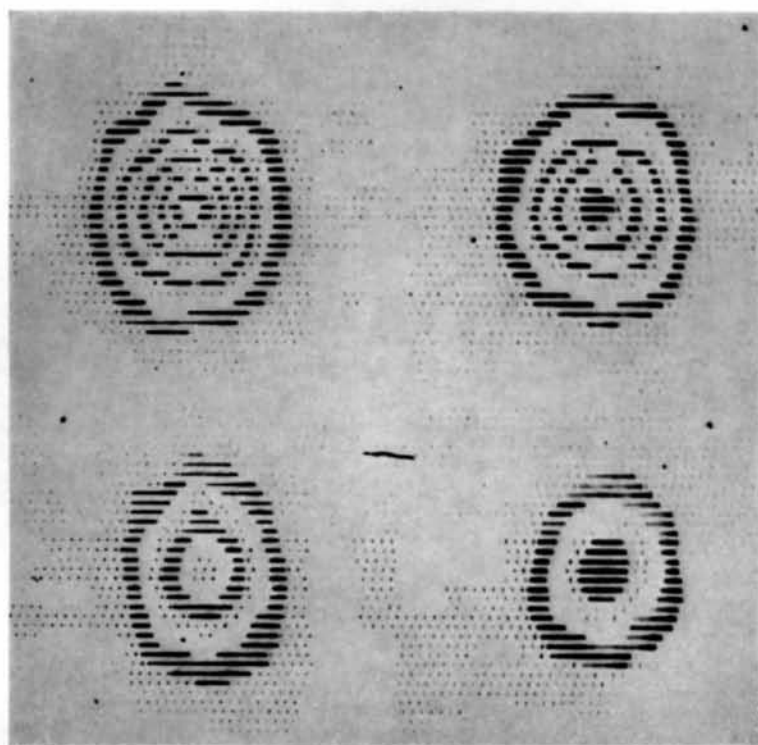

Fig. 1. Specimen-dependent properties of real crystals.

(a)

(b)

Fig. 2. Miniature film of olivine crystal, 0·9 Mg (multiple exposure on camera radius 1 cm) together with isodensitracer records of spot intensities (× 100) [R. Henriques & A. Graeme-Barber].
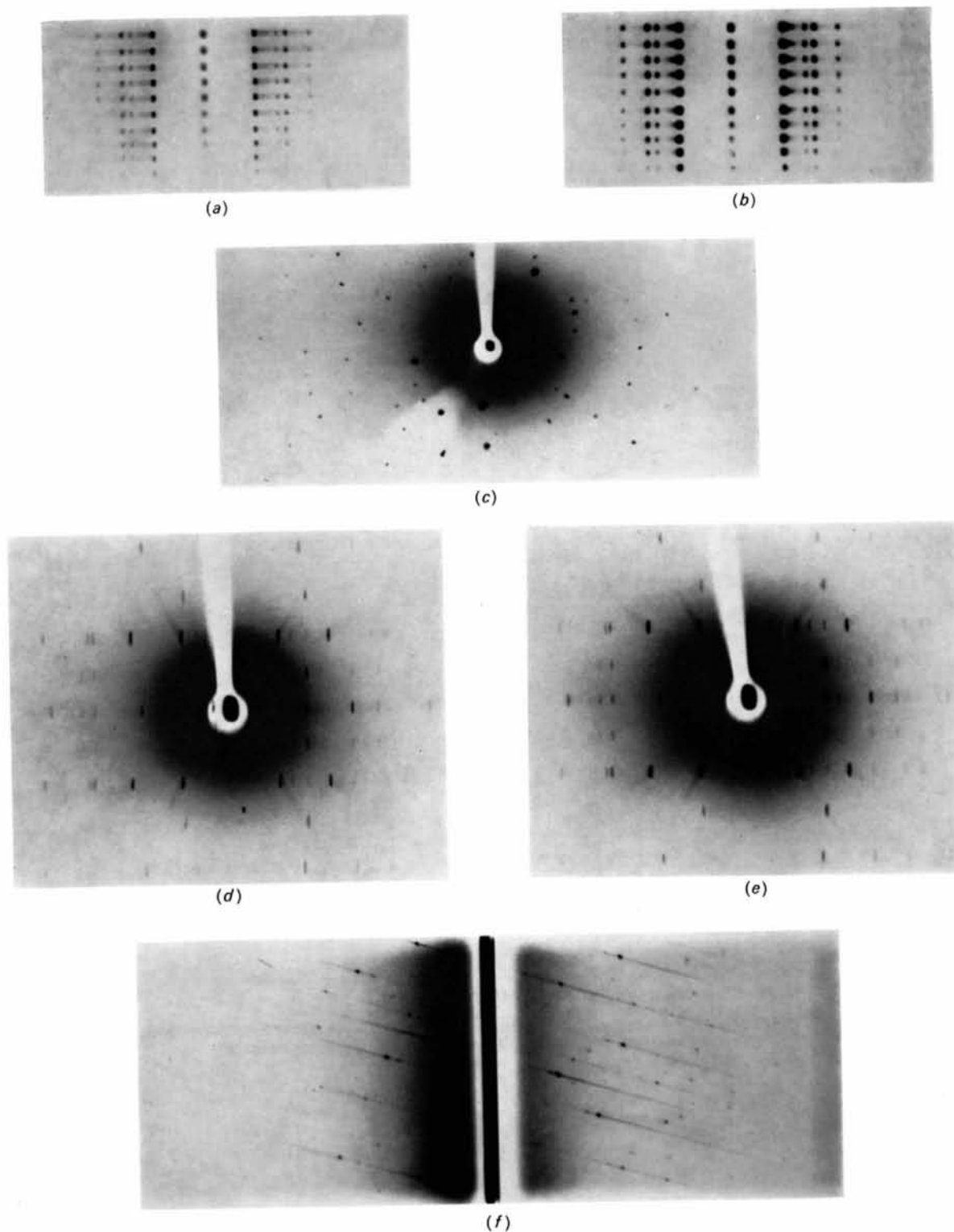
PLATE 20

Fig. 3. (a) Intensity scale on Ilford G film, made using Mo Kα and a urea crystal. (b) The same, using intensification with an Ilford A film. (c) Laue photograph, intensified, of a nickel olivine crystal 10μ thick (Mo target, 30 min exposure). (d) Ordinary 'integrated-oscillation' photograph of the same crystal. (e) Similar photograph, intensified, taken in half the time: Ilford Industrial A + Dupont Lightning-Special back screen. (f) Intensified Weissenberg of the same crystal, Mo K radiation, 11 hours exposure time [S. Devine].

cameras incorporate salt screens in good contact with normal Polaroid light-sensitive film in flat holders, and they have given acceptable intensification on precession cameras (which tend to be used with Mo radiation) or for Laue setting photographs (which contain a proportion of reflexions produced by very short wavelength X-rays). However, so far at we know, it has not proved possible to obtain Polaroid negatives coated on a transparent base so that they could be photometered in the usual way to permit intensity measurements to be made. Furthermore, Polaroid film is more expensive than ordinary X-ray film, and at present can only be used in flat film holders, so we have been experimenting with commercial X-ray film intended for use with intensifying screens. There seems to be considerable va iability amongst available film-screen combinations, but we find that Ilford Industrial A film in conjunction with a Dupont 'Lightning Special' back screen used with Mo $K\alpha$ radiation gives an intensification of about 6, and measurement of an intensity scale with a 0–3 density wedge on the Isodensitracer indicates that the intensification is essentially linear over this range. Fig. 3 shows 50° oscillation photographs (filtered, 4 hr integration parallel to the rotation axis) of a nickel-olivine crystal only 10 microns thick. It is not easy to tell by inspection which photographs of this crystal have been taken on Ilford Industrial G with long exposures (Fig. 3(d), and which using intensifying screens (Fig. 3(e)), and these results are so encouraging that although at present the corresponding results with Cu $K\alpha$ radiation are not satisfactory, it seems probable that really spectacular improvements could result from a vigorous attack on the whole problem of intensifying screens; and we ourselves intend to continue these tests.

Fig. 3(a) and (b) show corresponding intensity scales made with Ilford Industrial G film, and Ilford Industrial A and Lightning Special. Fig. 3(c) shows a Laue photograph, where the short wavelength reflexions show very large intensification, as does the quite small amount of hard radiation passing through the Pb beam trap in all these photographs. This is to be expected, since these screens are intended to provide optimum intensification at about 50-60 kV.

(b) Crystal shape

Crystal shape may be controlled during crystallization, or altered afterwards by cleaving or grinding, provided that a large enough specimen can be obtained in the first instance. The optimum shape is a sphere, which for crystals that are hard enough may be produced in a sphere grinder although in practice an ellipsoid is more often obtained because of the anisotropy of the abrasion resistance. This ellipsoid will in general exhibit the symmetry appropriate for the crystal system and this is particularly dangerous because it means that symmetry-related reflexions are often affected by systematic errors (such as absorption) where the necessary correction has the same symmetric properties as the

reflexion-sets themselves and internal consistency may give no indication at all as to the efficacy of the correction applied. Furthermore, because the symmetry is involved, the systematic errors can generally be absorbed by compensating errors in the ratios of $b_{11} : b_{22} : b_{33}$ where anisotropic temperature factors are applied, although the fact that absorption errors affect low-angle data preferentially, whereas thermal-ellipsoid anisotropy is mainly derived from high-angle data, means that the effects can often be disentangled on a difference Fourier (Jellinek, 1958), and by appropriate least-squares procedures.

In order to apply absorption corrections it is not only necessary to know the size and shape of the crystal (Jeffery & Rose, 1964), but also the value of the mass absorption coefficients involved. Many of the values listed by me in *International Tables* (1962) are quite inaccurate, often by as much as 5%, partly as a result of inadequate experimental data from which to interpolate values for all elements, and partly as a result of inadequate theory on which to base such interpolations. Better values are now in prospect, but if we assume that the radius of the sphere r can be measured to 2%, and that the linear absorption coefficient μ may be in error by 5%, then μr can be in error by about 7%.

These estimates of error certainly do not err on the high side; and when it is borne in mind that successive layers of data taken by the equi-inclination method especially for needle crystals are often corrected by means of cylindrical absorption corrections of the form $\mu t \sec v$, substantial systematic errors may actually be introduced in this way, and subsequently reflected in thermal ellipsoids showing marked anisotropy with respect to the needle axis; as such anisotropy was probably anticipated in any case, the error may well pass undetected.

It seems probable, therefore, that absorption errors may be greatly reduced by actually making measurements of the transmission fraction $I/I_0 = \exp(-\mu t)$, even in the case where the size and shape of the crystal can be quite accurately measured, since this is a situation where the precision of individual counter measurements can in fact be meaningful, assuming that I_0 is monochromatized by reflexion from a crystal or by use of a monochromator. An increasing number of empirical methods are being developed (see for example North, Phillips & Scott Mathews (1968)), especially for protein crystals, because in this case environment introduces additional complications.

(c) Environment

(i) Sample environment

Environment corrections include the effect of the adhesive used for mounting the crystal, or the matrix in which the crystal is located, windows in high- or low-temperature sample holders, air scattering and temperature fluctuations, and hence even barometric changes.

Consider first the adhesive. Generally a firm glue is chosen, which is used wet and allowed to dry. Most adhesives shrink appreciably on drying , and may exert quite sufficient force to distort a soft crystal. For example, Berry, van Horn & Griffith (1954) report that silver halide grains in ordinary X-ray film show lattice-constant values as much as 0·3 % below that expected, and that this concentration can be interpreted as being due to pressures approaching a kilobar due to the shrinkage of the gelatine on drying. I hope that it may be possible to exploit this phenomenon in high-pressure X-ray experiments, but in the present context it is intended as a warning that waxes may be much better mounting media than glues if distortion is to be avoided. We have confirmed that mixtures of Vaseline (petroleum jelly) (m.p. approximately room temperature) and beeswax (m.p. = 70 °C), in proportions adjusted to give the required viscosity, form an excellent mount, and in addition can be used to coat unstable crystals well enough to prolong their life sufficiently to permit data collection. 10% beeswax seems to give adequate stiffness for most purposes, and in addition Vaseline is a satisfactory mount for low-temperature work down to liquid-helium temperatures. Furthermore, since the wax does not harden, the crystal may be re-oriented at will.

The matrix in which the crystal is located may be natural (as in the case of mineral inclusions in diamond), or artificial, as in the case of low-temperature experiments for example, where the crystal has to be kept under conditions other than R.T.P. In either case the effects of the matrix can be effectively minimized or, by paying careful attention to collimation on, occasions even turned to advantage (Fig. 4). This is the case for protein crystals, where instability (see section (e) below) dictates that the crystal must be kept in a liquid. This requirement has been brilliantly exploited in the development of the flow-cell (Wykoff, Doscher, Tsernoglou, Inagami, Johnson, Hardman, Allewell, Kelly & Richards, 1967) in which the composition of the liquid is changed so that the heavy-atom content of the crystal also changes, and 'isomorphous-series' measurements are made from one individual crystal by varying its composition during the course of data collection.

The complex nature of artificial environments generally makes empirical absorption corrections of the kind already cited the only procedure which is really feasible.

(ii) *Reflexion environment*

It is convenient to consider here the problem of the thermal diffuse scattering which rises to a maximum under the Bragg reflexion. The intensity distribution is largely dependent on the elastic constants of the crystal, and may thus in some cases be used to measure them. Alternatively, if the elastic constants are known, isodiffusion surfaces may be calculated at least approximately, as was done for sodium (Lonsdale, 1942).

Fig. 5 shows an isodensitracer measurement of the 002 reflexion on a stationary-crystal photograph of sodium taken with virtually monochromatic Cu Kα radiation (cf. Plate 6(a), Lonsdale, 1942). Lonsdale compared the diffuse shape on the photograph with the corresponding isodiffusion surface calculated from the available elastic constants using equations due to Jahn (1942). It would be easy to produce such isodiffusion surfaces using a computer-controlled graph-plotter, and it seems to be worth while to explore the possibility of obtaining the necessary corrections in the vicinity of Bragg reflexions directly from careful studies of the intensity distribution on suitable stationary-crystal photographs.

The environment of reflexions may be further complicated by diffuse effects due to disorder or short-range order of various kinds. Such effects are usually immediately apparent on X-ray photographs (especially on stationary-crystal photographs), and can generally be recognized as anomalous even by relatively unskilled investigators. With diffractometers, however, which only sample carefully selected regions of reciprocal space, it is questionable whether effects of this kind can be reliably detected without resort to quite elaborate and time-consuming procedures. The tacit recognition of the myopia of such instruments is implicit in the rather widespread practice of taking photographs of a crystal before using it for diffractometry.

(d) Homogeneity

(i) *Physical homogeneity*

This can be considered at two levels; firstly gross inhomogeneity, which results in the distortion or extension of reflexions to such a degree that the measurement of their integrated intensities presents considerable problems in itself; and secondly on the presence or absence of mosaicity on a sub-microscopic scale, which does not lead to appreciable visible alteration of the X-ray reflexions, but which may profoundly affect their intensities through the phenomenon known as extinction.

An example of the first type is shown in Fig. 6(a) (c) (d) and (e). It would not really be feasible to measure these reflexions even with an integrating densitometer, but as Fig. 6(b) and (f) show, use of an integrating mechanism on the *camera* instead of on the densitometer produces quite acceptable results. It may be possible to devise equivalent diffractometer procedures, but photographic scanning techniques of this kind involve relatively cheap and simple mechanical alterations to standard X-ray cameras, and have such large advantages for poorly crystallized material that many forgotten integrating mechanisms on Weissenberg cameras might very profitably be resuscitated, and used to obtain integrated-oscillation photographs Milledge, to be published).

Detailed representation of the reflecting power of a crystal may be obtained from various types of X-ray
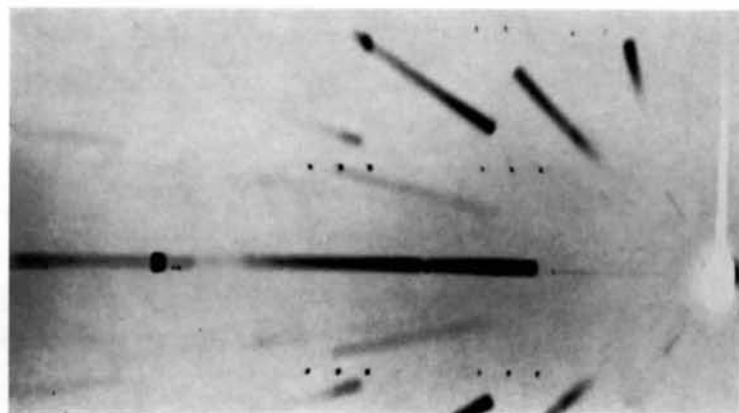
(a)
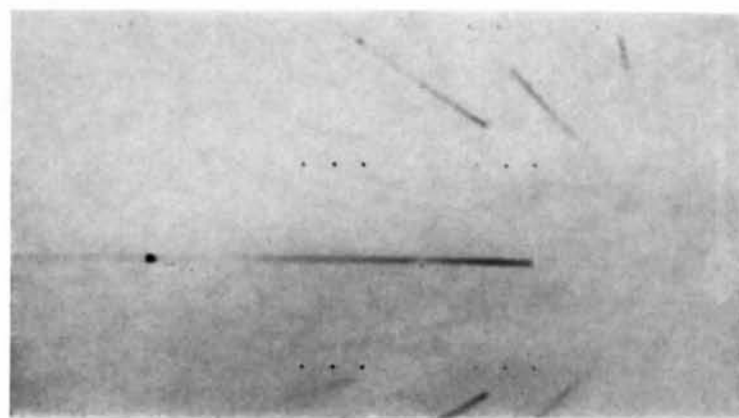
(b)

Fig. 4. Oscillation photograph, using Cu K radiation, of a diamond containing a small enstatite inclusion. (a) Using a 1 mm diameter collimator. (b) Using a $\frac{1}{2}$ mm diameter collimator [R. Henriques].
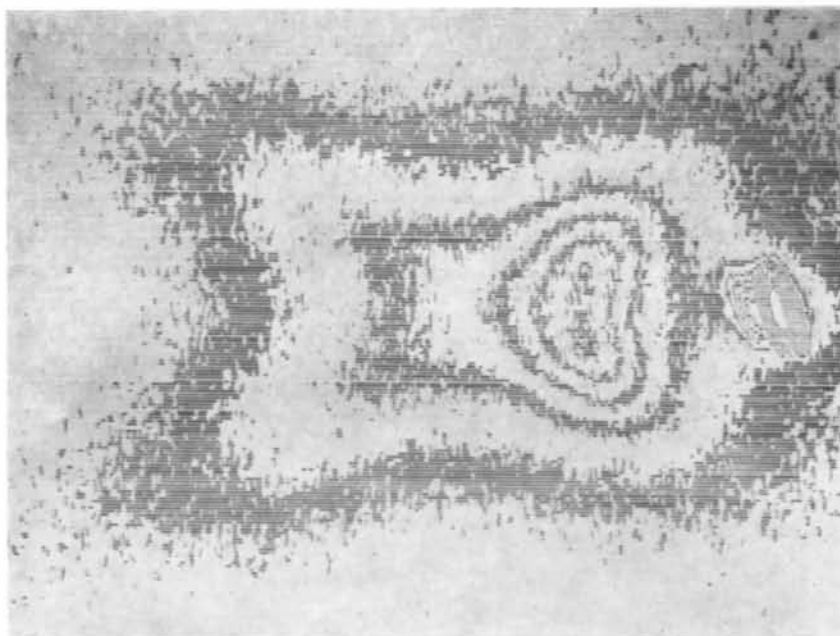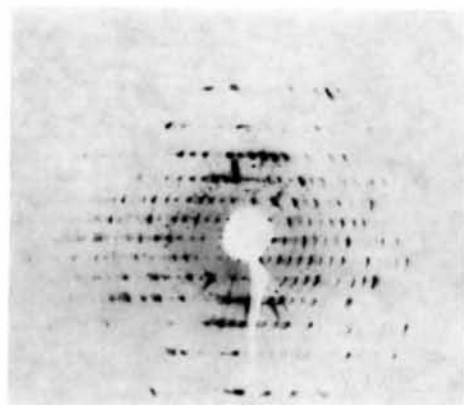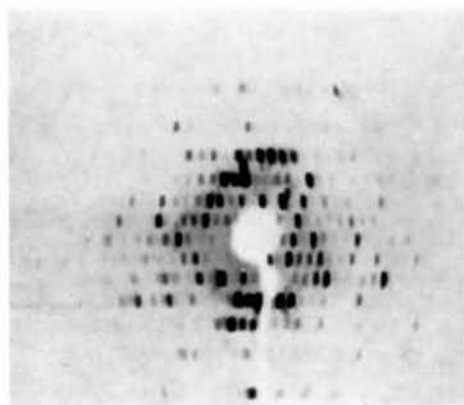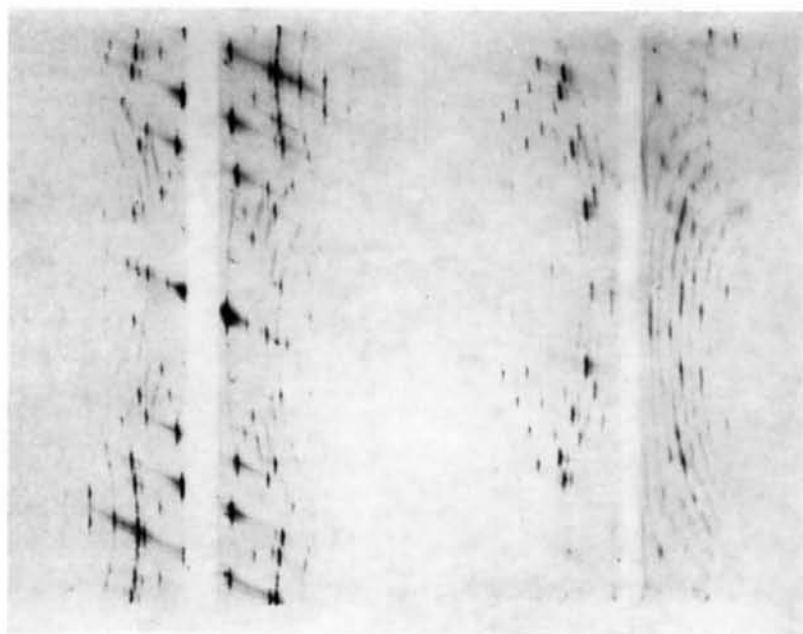
Fig. 5. Isodensitracer record of 002 diffuse + Laue reflexions on a stationary-crystal photograph of sodium, using radiation from a Cu target (*cf.* Lonsdale, 1942) [A. Graeme-Barber].
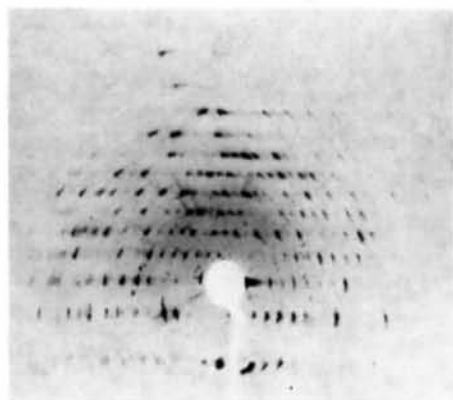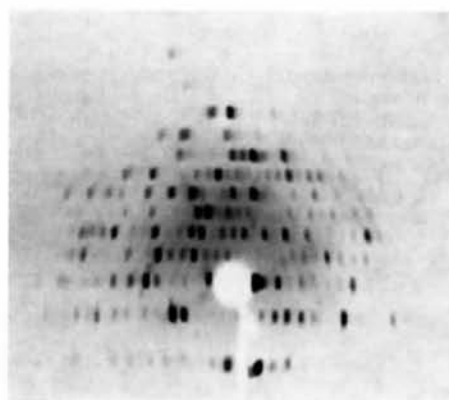
Fig. 6. (a) Oscillation photograph of a badly-distorted crystal of tetramethylrubrene. Normal-beam, Cu $K\alpha$ radiation. (b) The same, integrated. (c) Zero-layer Weissenberg, not integrated. (d) First-layer Weissenberg, not integrated. (e) Inclined-beam oscillation photograph, not integrated. (f) The same, integrated [E. Hoff].
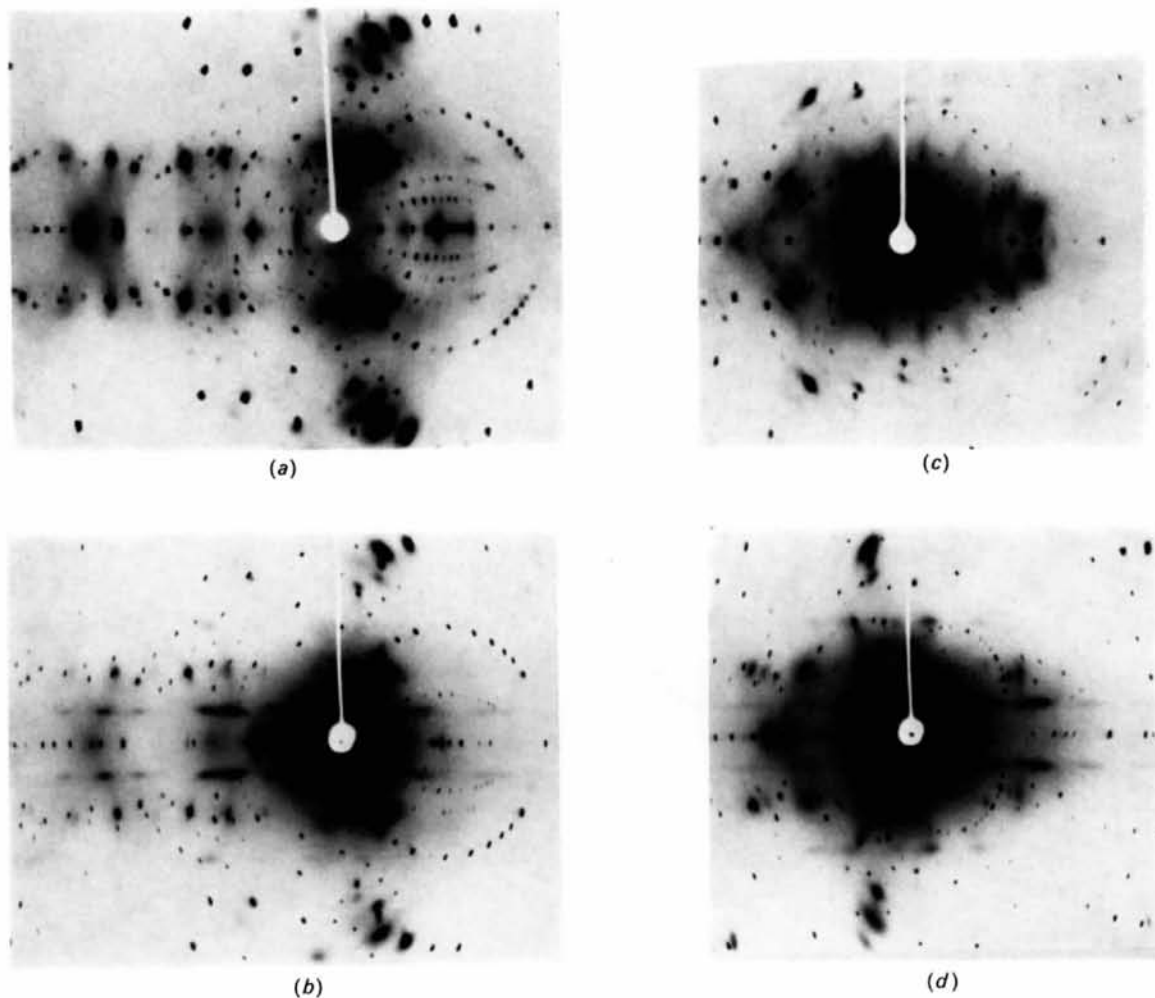
Fig. 7. (a) Stationary-crystal photograph, cylindrical camera, using radiation from a Cu target, of anthraquinone, b axis vertical, showing strong diffuse thermal scattering. (b) A similar photograph of the isostructural anthrone, in a similar orientation, showing additional 'layer-line' diffuse scattering, due to short-range order, at $b = \pm \frac{1}{2}, \pm \frac{3}{2}$. (c) A comparable photograph of N-oxyphenazine showing thermal scattering + short-range order scattering, the latter however being along a-constant row-lines $a = \pm \left(\frac{2n+1}{2} \right)$. (d) A similar photograph of anthrone, in a similar orientation, but with short-range order diffuse scattering, as in (b), along b-constant layer lines [H. D. Flack & A. M. Glazer].

topographs (for example Frank & Lang 1965). Given the necessary equipment, such topographs are neither difficult nor time-consuming to prepare, though in general they have been employed for the investigation of crystals much larger than those normally used for intensity measurements needed in structure determination. The method does, however, have something in common with the use of very fine slits in diffractometry to obtain high-resolution results of various kinds, and the ease with which dental films can be placed anywhere without the need for special film-holders does suggest simple practical tests for homogeneity for diffractometer users, quite apart from the pre-eminence of the technique in its own sphere.

Assuming that the mosaic spread is of interest, it may be noted that multiple reflexions are extremely texture-sensitive (Renninger, 1955). The four-circle diffractometer is a particularly suitable instrument for making such measurements, since multiple-reflexion measurements require that a set of planes (hkl) should be brought into the reflecting position and then that the crystal be rotated about the normal to this set of planes; and this can generally be arranged with the available controls. It should further be noted that the angular distribution of double-reflexions about the normal is extremely sensitive to lattice parameter variations in favourable cases (Isherwood & Wallace, 1966), and could well be exploited to obtain accurate lattice parameters.

(ii) Chemical homogeneity

This is likely to be a particular problem in non-stoichometric compounds, and in variable-composition systems such as many minerals, or mixed-crystal systems and solid solutions. The homogeneity is likely to be influenced by crystal origin (melt or solvent) time-temperature route of crystallization, impurities, subsequent history etc. and is very likely to be specimen-dependent. In some cases homogeneity can now be investigated down to a resolution of about one micron by using a microprobe (which is essentially an X-ray surface reflexion technique and critically dependent on available mass-absorption corrections) or occasionally by absorption topography (which is an X-ray bulk-specimen technique also dependent on mass-absorption corrections), as in the case of banded amethyst (Schlössin & Lang, 1965). Both techniques have a resolution of the order of 10^4 atoms, and hence leave a large and currently unbridged gap between such relatively gross inhomogeneities and short-range order, where cooperative phenomena extending over a few unit cells give rise to well known diffuse phenomena in alloys, and sometimes in organic crystals. For example, Fig. 7 shows stationary-crystal photographs of the centrosymmetric anthraquinone and of anthrone, which is pseudo-centrosymmetric. In fact the corresponding thermal diffuse effects are of approximately similar intensity, but the anthrone has been less exposed because of the intensity of the strong half-

layer-line scattering which is due to short-range order (Flack, 1968). N-Oxyphenazine (Glazer, 1968) is also pseudo-centrosymmetric, but the short range order in this case is differently orientated.

Such phenomena do not, however, generally interfere with the collection of data for structure determination, but merely serve to indicate that the resulting atomic positions, site-occupation electron counts, and in particular the apparent thermal-motion parameters, should be interpreted with the greatest care, as they may represent various types of space-average of several discrete structures rather than an average uniform cell.

One practical problem which does arise in this context is the application of calculated absorption corrections, because if the chemical composition is unknown, as may be the case in site occupation studies where the determination of exact composition is the object of the experiment, the appropriate absorption coefficient is unknown, and, by definition, measurements of the absorption may actually be useful in determining the chemical composition (Henriques & Milledge, to be published). This again emphasizes the necessity for an intelligent choice of data to be measured, since in this type of problem it usually happens that a few reflexions are extremely sensitive to the parameters in question so that careful measurements of selected reflexions will be much more valuable than painstaking collection of all reflexions which can be located. It is not only possible but extremely sensible to compute the expected intensities before any data is collected at all, so that an optimum choice of radiation, orientation and parameter-sensitive reflexions can be made in advance. We are currently exploring the usefulness of this type of analysis in determining the chemical composition of mineral inclusions in diamond (Harris, 1968; Henriques, 1969). A result of some interest in this connexion is that for rotation about a cubic [111] axis, at least 3 reflexions which are equivalent by definition $(hkl \circlearrowleft)$ are always superposed, and data sets from such rotation photographs showed better shaped reflexions and noticeably better internal consistency than was achieved for individual oscillation photographs of the same crystal, a result we had previously observed for hexamine.

(e) Stability

Stability is probably the most important consideration of all, since in general a good value of any intensity may be obtained by taking enough trouble, which usually means enough time. It is especially important in diffractometry, where measurements are made serially, and it is important to eliminate spurious indications of instability which merely represent detector fatigue. Some such precaution is essential when unstable materials are the main object of study, since the general practice of periodically re-measuring one or more 'standard reflexions' is not applicable in this case. The problem of instability may be tackled by speeding

up the measurements or by slowing down the rate of change. Measurements may be speeded up by using image intensifiers with diffractometers, or intensifying screens with X-ray film, or by populating films more efficiently by collecting the data without screens. In the case of films, however, it is very simple to *collect* data at a much higher rate than that at which it can be *extracted* from the films without resorting to quite elaborate procedures, so that although photography is the most satisfactory way of recording data in unstable situations, it is unlikely to become generally popular until computer-controlled densitometers are moie generally available to produce immediate numerical results, which is one of the attractions of diffractometry.

In order to overcome the problem of instability of the detector and/or counting-chain, we have incorporated an iron-55 source in one of the two tape-controlled filter wheels in our diffractometer. This is plated onto a brass disc, and contains enough of the isotope to give a signal of about 100 c.p.s. It is not ideal, because its energy is about 5·9 kV, whereas the value for Cu $K\alpha$ is about 8·5 kV, and hence the window of a pulse-height analyser must be set wider than is really desirable. Furthermore, the half-life of ^{55}Fe is really shorter than one would like for use over several months or years. Nevertheless it is extremely useful, and it is of interest that it is now possible to obtain ^{193}Pt in liquid form so that it may be plated in the same way. Here the energy is much better matched to Cu radiation, being 9·15 kV ($\lambda = 1·35$ Å) and the half-life is about 500 years, so that although this is so expensive that a strong enough source for monitoring purposes might be comparable in cost with a good detector, the fact that for all practical purposes it would be a permanent standard in a given laboratory makes it seem worthwhile, and we are now plating a ^{193}Pt disc for testing.

Considering now the crystal itself, there are two separate problems, stability with respect to environment and stability with respect to radiation. The environment problem is likely to be highly specific to the experimental procedure actually in use, but stability with respect to radiation is a much more serious problem. It is often suggested that data should be taken at low temperatures to reduce instability, but it is worth noting that much less self-annealing is likely to occur at lower temperatures so that damage at low temperatures is permanent, until the temperature is raised.

In one case that has been studied in this laboratory (Lonsdale, Nave & Stephens, 1966) X-radiation and heat seem to produce exactly the same type of instability. The photo-oxide of anthracene decomposes to a mixed crystal of anthraquinone and anthrone, the speed of the reaction depending sharply upon the temperature. At room temperatures a normal X-ray exposure of only a few hours produces changes in the intensity, with the appearance of short-range order streaks, that are obvious on certain types of X-ray photograph but not on others.

It must not, however, be assumed that observed instability (other than chemical combination with the oxygen, water *etc.* of the atmosphere) is in fact caused by the X-radiation used. It is possible for light, visible or ultraviolet, to act in this way and for the reaction involved to be reversible but the damage caused not necessarily to be self-annealing, so that the texture may deteriorate. A particularly interesting case occurs for anthracene, which was formerly supposed not to dimerize in ultraviolet (although it obviously deteriorates on prolonged exposure to X-radiation, for example if used as a monochromator). However, it has recently been shown (O'Donnell, 1968) that when the ultraviolet is filtered through Pyrex so that part of the spectrum is removed, extensive dimerization of anthracene does occur. Such phenomena, therefore, are highly wave-length specific and the composition of a laboratory window in a sunny climate or of the envelope of a laboratory lamp may influence the stability of the crystal.

Summary and conclusions

Specimen-dependent properties of real crystals influence the accuracy with which intensities can be measured, and may not be controllable.

Size and shape may be controlled (sometimes) during or after crystallization. Absorption corrections may in principle be applied accurately, provided that the size and shape of the crystal can be determined accurately, and that the absorption coefficients for the elements involved are known accurately. It is possible that experimental determination of the combined quantity μt actually occurring in the exponential for the radiation concerned may give better results than attempts to obtain both separately.

Spot-shape corrections may again be applied accurately in principle, but it is possible that integrated intensity measurements may be almost as good as or better than elaborate correction of poor data.

In contrast to size and shape corrections, which may be considered as theoretical corrections, at least in principle, environment corrections are necessarily experimental and will normally depend on the procedures in use in any particular laboratory; they are more likely to affect comparisons of absolute intensities than relative ones.

Homogeneity may be influenced by crystal origin (melt, solvent, time-temperature route of crystallization, impurities, subsequent history, *etc.*) and can only be determined by experiment. The two most important effects in this category are disorder, and texture as it affects extinction. The most simple and informative diffraction test is a well-exposed Laue photograph taken with characteristic + continuous radiation, which will reveal distortion or inhomogeneity in the spots themselves, and will often show diffuse effects indicative of disorder. Two types of test are required; uniformity of symmetry-related reflexions, and compar-

ative measurements on different specimens. It is questionable whether excellent results on a single specimen really give much information about a particular chemical compound, whose behaviour is quite as important as its constitution. Now that it is possible to obtain X-ray topographs, it may be that specimens suitable for problems of particulai interest could be selected in this way.

Inhomogeneity is a particular difficulty in variable-composition crystals such as minerals and ferrites, where it is likely to be chemical rather than physical.

The most important problem of all is probably instability. In addition to incorporating periodic checks on the stability of the detector and its circuitry, this problem may be tackled by speeding up the measurements or slowing down the rate of change. Thus instability with respect to the environment may be overcome by coating the crystal, or placing it in a tube containing liquid or vapour. This approach has recently been particularly fruitful for proteins. Some experiments with wax mixtures of variable viscosity have been made. Instability with respect to radiation can sometimes be overcome by lowering the temperature, but care should be exercised here, as no significant amount of self-annealing is possible at low temperatures.

The best solution is rapid measuiement, and several new photographic techniques are now available. Some give 'good' films from 'bad' crystals.

It often happens that when a special effect in a real crystal is large enough to be a real nuisance from the structure-analysis point of view, the effect is worth studying for its own sake.

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DISCUSSION

MEZ: Dr Milledge's view of the possibility of observing changes in crystals during an intensity collection run on a diffractometer seems overly pessimistic. From our own experience, the small changes in the cell constants which are bound to result from such a change become very manifest in the positions of individual reflexions. This effect is easily seen in the output of a properly organized data collection routine.

We have observed a solid-state photopolymerization effect on the diffractometer which did not occur on the Weissenberg camera after seven days of exposure. The polymerization was obviously started by the combination of X-rays and artificial lighting, and the change in cell constants was seen from scan data after some ten hours exposure. Subsequent Weissenberg photographs confirmed a slight degree of decomposition in the crystals.

MILLEDGE: It depends very much on the specific circumstances. In many cases of organic compounds, there is not much evidence of alteration in the main phase to be gained from changes in its own reflexions. However, evidence concerning the new phase may be building up in other, different regions of reciprocal space. The problem is that, with the diffractometer, one may not be aware of the situation whereas with films it makes itself obvious.

LADELL: One can use the diffractometer to study three-dimensional sections of reciprocal space, just as one uses film. It is only necessary to program the control to carry out this procedure.

FURNAS: (a) The point is well made, but we should recognize that a diffractometer exploration of reciprocal space, being sequential in time, does differ from the averaging process of film. Changes may well occur during the process of diffractometer search.

(b) Another point to note is that, if you do collect both film and counter data, be sure to compare them very carefully to establish a check.

HAMILTON: Even for a complicated structure, it is advisable if possible to aim for 1% accuracy rather than 5%, since it may aid in facilitating the analysis and yet probably does not cost much extra work.

MILLEDGE: I do not agree with this viewpoint. Particularly where special attachments are concerned *e.g.* for low or high temperatures, film procedures are far more adaptable. Also I would question whether your nominal 1% accuracy is really being achieved.

HAHN: There is also the alternative situation when you only get 5% and need 1%.

SANDOR: The incorporation of an iron-55 radioactive source in an automatic X-ray diffractometer is designed for checking the stability of the counting chain at regular intervals. Do you not think that it would be advisable to keep a similar

check on the stability of the primary X-ray beam as well? Alternatively, do you have any experimental evidence which would indicate that fluctuations in the primary X-ray beam produced by a stabilized X-ray generator are negligible compared with other sources of instability over the period of data collection?

MILLEDGE: One notes in the report on the I.U.Cr. Single Crystal Project that the X-ray generators appear to have, in some cases, poor long-term stability, as measured by the radiation detector. My own opinion is that the X-ray tubes themselves are probably as stable as the manufacturers claim

but that the instabilities and drifts probably arise in the quantum counting system. It was for this reason that I suggested the use of a radioactive source to check this item.

ABRAHAMSSON: It is necessary to consider the duration of the experiment which may be quite different by film and diffractometer methods.

RIVA DE SANSAVERINO: It may be of minor statistical interest that in *Acta Crystallographica* for 1966, admittedly not 1968, the ratio of structures done by film procedures relative to those by diffractometry was 4:1.

F2·1

Errors in the Calculated Structure Factors Caused by the Free-Atom Form Factor Model*

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The excellent agreement often obtained in least-squares refinement of X-ray data with the free-atom form factor model suggests that deviations from sphericity are small. However, the resulting parameters are affected by bonding effects to a small but significant extent. In the present paper, errors in F_{calc} are defined as differences between the free-atom structure factors calculated with the true atomic parameters and those which would be obtained from an exact description of the electron density. An experimental measure of these errors can be obtained from the parameters determined independently by neutron diffraction. The structure factor errors for s-triazine and α-deutero-oxalic acid dideuterate are analyzed and contrasted with errors in form factors resulting from neglect of overlap density, prepared state and orbital contraction. The theoretical curves indicate that deviations from the free-atom model persist at values of $\sin\theta/\lambda$ larger than 0·6 Å⁻¹. Improved models for molecular scattering based on valence bond and molecular orbital theories respectively, are discussed. The importance of errors in neutron scattering lengths is demonstrated by least-squares refinements of α-deutero-oxalic acid with various values of b_D. Good agreement between F_{obs} and F_{calc} is obtained at the expense of systematic deviations in the deuteron temperature factors. Finally a summary is given of the errors in X-ray parameters obtained by least-squares adjustment with the free-atom model.

Introduction

In the last few years quite a few structures have been published for which excellent agreement of 5% or better between calculated and observed intensities has been obtained by the use of the free-atom spherical form factor model. The results of such analyses suggest that spherical atoms are a close approximation to bonded atoms in molecules. However, the least-squares refinement through which this agreement is obtained is designed to give a best fit between experiment and calculations. As a result, the final least-squares parameters are affected by the choice of model to an extent not necessarily reflected in the standard deviations or the agreement factors derived. For the present purpose, we shall define the errors in F_{calc} as the differences between the spherical atom structure factors calculated with true positional and temperature para-

meters and the true structure factors which would be calculated with the same parameters and an exact description of the electron density distribution. These errors in F_{calc} are appreciably larger than the experimental errors associated with advanced data collection techniques.

Experimental estimate of the errors in F_{calc}

Observed X-ray structure factors are an experimental measure of the true F's with a superimposed effect of thermal motion. The comparable spherical structure factors can be obtained when positional and thermal parameters have been measured independently in a neutron diffraction experiment. Such experiments have been performed at room temperature for a small number of compounds among which s-triazine (Coppens, 1967) and α-deutero-oxalic acid dideuterate (Coppens Sabine, Delaplane & Ibers, to be published). A similar analysis on cyanuric acid at liquid nitrogen temperature may be affected by small differences in data collection temperatures, and will be discussed elsewhere (Coppens

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