The coefficients of the third-cumulant tensor should provide additional data for interpreting the thermal motion of molecules in terms of the rigid-body model. Further work along this line is planned.

A more detailed analysis of the cumulant expansion model will be published elsewhere (Johnson, 1969).

I gratefully acknowledge the stimulating discussions with my colleagues H. A. Levy and W. R. Busing which led to the cumulant expansion model. The assistance of V. R. R. Uppuluri with the Edgeworth series expansion was also invaluable. Thanks are due to G. M. Brown for discussions on copper acetate monohydrate and for the use of his unpublished neutron data, and to E. N. Maslen for a preprint of his manuscript on thermal motion.

DISCUSSION

See page 204.

References

Birss, R. R. (1964). *Selected Topics in Solid State Physics*, Vol. III. *Symmetry and Magnetism*. Amsterdam: North-Holland.

Brown, G. M. & Chidambaram, R. (1967). American Crystallographic Association Winter Meeting, Atlanta, Georgia, Abstract A10.

Burns, J. H., Agron, P. A. & Levy, H. A. (1963). *Noble-Gas Compounds*, Ed. H. H. Hyman, p. 211, Chicago: Univ. of Chicago Press.

Chambers, J. M. (1967). *Biometrika* **54**, 367.

Chidambaram, R. & Brown, G. M. (1969). To be published.

Cramér, H. (1946). *Mathematical Methods of Statistics*. Princeton: Princeton Univ. Press.

Dawson, B. (1967). *Proc. Roy Soc.* A**298**, 255.

Dawson, B., Hurley, A. C. & Maslen, V. W. (1967). *Proc. Roy. Soc.* A**298**, 289.

Edgeworth, F. Y. (1905). *Proc. Camb. Phil. Soc.* **20**, 36.

Forsythe, G. & Moler, C. B. (1967). *Computer Solution of Linear Algebraic Systems*, Chap. 25, Englewood Cliffs: Prentice-Hall.

Gnedenko, B. V. & Kolmogorov, A. N. (1954). *Limit Distributions for Sums of Independent Random Variables*. Cambridge: Addison-Wesley.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502.

Higman, B. (1955). *Applied Group-Theoretic and Matrix Methods*. London: Oxford Univ. Press.

Johnson, C. K. (1965). Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Johnson, C. K. (1969). *Measurement and Interpretation of Accurate Neutron Structure Factors*, Edited by B. T. M. Willis. London: Oxford Univ. Press. In the press.

Kendall & Stuart, (1958). *The Advanced Theory of Statistics*, Vol. I. London: Charles Griffin.

Rouse, K. D., Willis, B. T. M. & Pryor, A. W. (1968). *Acta Cryst.* B**24**, 117.

Sirotin, Y. I. (1960*a*). *Soviet Physics-Cryst.* **5**, 157.

Sirotin, Y. I. (1960*b*). *Soviet Physics-Doklady*, **5**, 774.

Sirotin, Y. I. (1961). *Soviet Physics-Cryst.* **6**, 263.

Sirotin, Y. I. (1964). *Soviet Physics-Doklady*, **8**, 652.

Tu, Y. O. (1968). *Acta Cryst.* A**24**, 273.

Vos, A. & Johnson, C. K. (1969). To be published.

Wallace, D. L. (1958). *Ann. Math. Statist.* **29**, 635.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558.

Acta Cryst. (1969). A**25**, 194 F2·3

Comparison of X-Ray and Neutron Diffraction Structural Results: A Study in Methods of Error Analysis*

By Walter C. Hamilton

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

A number of crystal structures have been precisely analyzed by both X-ray and neutron diffraction. Comparison between the results can lead to some understanding of the type and magnitude of error present in one or both methods. We discuss here the nature of systematic error in crystallographic experiments and in crystal structure refinement models. Statistical methods are presented for testing the significance of the difference between the parameters derived in two crystallographic experiments. These methods are applied to existing neutron and X-ray diffraction data on oxalic acid dihydrate, hydroxyapatite, *s*-triazine, potassium hydrogen diaspirinate and methylglyoxal bisguanylhydrazone. These tests show that there are strong systematic differences in thermal parameters for heavy atoms and in all parameters for hydrogen atoms. Differences in positional parameters for heavy atoms are marginal. The pattern of results strongly suggests that the differences between neutron and X-ray experiments have some physical basis rather than being due entirely to systematic error in one or both experiments. The results may also be interpreted as indicating that both position parameters and root-mean-square amplitudes of vibration may with care be determined to a precision of 0·001 Å and an accuracy of 0·005 Å in structures with a moderate number of atoms in the asymmetric unit.

Introduction

In the experimental part of the classical crystallographic diffraction experiment, an attempt is made to measure the magnitude of the structure factor $|F|$, where F is the Fourier transform of the contents of one unit cell of the crystal:

$$F(\mathbf{h}) = \int_{\text{cell}} \varrho(\mathbf{r}) \exp (2\pi i\mathbf{h} \,.\, \mathbf{r})d\mathbf{r} \,. \tag{1}$$

---

* Research carried out at Brookhaven National Laboratory under contract with the U. S. Atomic Energy Commission.

Failure to achieve the aim of exact determination of this quantity for all accessible values of the reciprocal lattice vector **h** may be called *experimental error*. The examination of the possible sources of this error is the main topic of this meeting.

In the interpretational part of the classical crystallographic diffraction experiment, the set of measurements $\{F(\mathbf{h})\}$ is fitted to a particular physico-chemical model. This model usually assumes that the structure factor may be written as a sum of contributions from the N individual atoms in the unit cell:

$$F(\mathbf{h}) = \sum_{i=1}^{N} f_i(\mathbf{h}) T_i(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_i) , \quad (2)$$

where $f_i(\mathbf{h})$ is the atomic scattering amplitude – the Fourier transform of the scattering density of a hypothetical motionless atom which is otherwise identical to the atom in the real crystal. $T_i(\mathbf{h})$ is the Debye–Waller factor – the Fourier transform of the probability function for the position of the center of the atom with respect to its mean position $\mathbf{r}_i$. Given sufficient generality in the forms $f_i(\mathbf{h})$ and $T_i(\mathbf{h})$, the model implied by (2) is also perfectly general in that any function of **h** may be so described. The usefulness of model (2) is of course that, to a good degree of approximation, real crystals may be described by especially simple functions $f_i(\mathbf{h})$ and $T_i(\mathbf{h})$, each containing certain parameters to be determined from experiment. In most routine crystallographic experiments, $f_i(\mathbf{h})$ is assumed to be the spherically symmetric function characteristic of the free atom, and $T_i(\mathbf{h})$ is assumed to be a centrosymmetric three-dimensional normal probability function. Interesting departures from these simple models have been discussed in other papers at this meeting. The refinement of parameters under the assumption of an incorrect model may be called a *theoretical error*.

Since neutron and X-ray diffraction experiments are carried out in the attempt to attain the same kinds of information, it is interesting to compare results between the two techniques. The difference between the two techniques lies in the fact that in (1), $\varrho(\mathbf{r})$, to a very high degree of approximation, is the motionally averaged electron density in the X-ray experiment, and is the motionally averaged nuclear density in the neutron experiment. In terms of the general model (2), $f_i(\mathbf{h})$ is a constant characteristic only of properties of the nucleus for the neutron experiment but is at best a decreasing function of $|\mathbf{h}|$ for the X-ray experiment and may have more complex behavior. Again, $T_i(\mathbf{h})$ will reflect the effect of vibrational motion of the electron density in the X-ray case and on the nuclear positions in the neutron case. The mean atomic position $\mathbf{r}_i$ is not well-defined in either case but depends upon the model that is chosen for $T_i(\mathbf{h})$ and $f_i(\mathbf{h})$.

Despite the reservations in the previous two sentences, any comparison between a neutron diffraction experiment and an X-ray diffraction experiment is generally made in terms of the mean atomic positions $\mathbf{r}_i$ and the detailed description of the Debye–Waller factors $T_i(\mathbf{h})$. This paper is concerned with an attempt to understand what such comparisons can tell us about

(i) possible experimental errors,
(ii) possible theoretical errors,
(iii) the physics and chemistry contained in the parameters of the model.

Errors in measurement

The terms *systematic error* and *random error* are very often used without their precise meanings being understood; indeed they are used with different meanings in different contexts. On one level, one might be tempted to say that the random error in an X-ray diffractometric experiment is that due to the uncertainty induced by the measurement, for a finite time span, of events governed by a Poisson distribution – 'counting statistics'; all other sources of variation in measurement would be ascribed to systematic error since they are presumably related to faulty techniques of measurement which can be corrected. Assumption of this definition has led some workers in the field to assume that the weights in a least-squares analysis should be taken as inversely proportional to the variances derived from counting statistics alone; this misapprehension can lead to disaster.*

A more useful definition of systematic error is that associated with the statistical concept known as *bias*. If we carry out a measurement in such a way that it may be repeated many times, each measurement of a quantity whose true value is F_0 may result in a value

$$F_i = F_0 + \Delta F_i . \quad (3)$$

The error ΔF_i will vary from measurement to measurement. It may be assumed to be drawn from a population of possible values described by some probability distribution function $\varrho(\Delta F)$. If the mean value of ΔF,

$$\mu(\Delta F) = \int \Delta F \varrho(\Delta F) d(\Delta F) , \quad (4)$$

is zero, then it follows that the mean value of F_i is given by

$$\mu(F_i) = F_0 ; \quad (5)$$

that is, the mean or expected value of the measurement is the true value F_0, and the measurement is said to be *unbiased. There is no systematic error.* On the other hand, if the mean value of ΔF is some non-zero quantity $\mathscr{S}$, we find that

$$\mu(F_i) = F_0 + \mathscr{S} . \quad (6)$$

The quantity $\mathscr{S}$ is the *bias* or *systematic error.* No matter how many measurements we make of F, we can

---

* It is equally true that agreement among equivalent reflections is not necessarily a satisfactory basis for a weighting scheme.

only hope to converge to a good value for $F_0+\mathscr{S}$, not for F_0 alone.

On the other hand, the statement that there is a probability distribution associated with ΔF is a statement that there is random error present. If there were not, a measurement of F would always result in F_0. In the strict sense, random error need not be unbiased and thus includes the systematic error as defined above. In the present discussion, it is useful and is also common practice among crystallographers to restrict *random error* to that component of the error which shows no bias. One suitable measure of the random error is the variance of ΔF:

$$\sigma^2(\Delta F)=\int(\Delta F)^2\varrho(\Delta F)d(\Delta F)-\mu^2(\Delta F)\,. \tag{7}$$

It is important to note that there may be many uncertainties in the experiment which can lead to large unbiased random errors. Aside from Poisson counting statistics there may be fluctuations in the intensity of the incident radiation, noise in the counting circuitry and mechanical vibrations. Such sources of error – and there are others in the same class – may be expected to be suitably random over the course of data collection from a single crystal.

But there may also be variable factors associated with the individual crystal. The crystal perfection may vary, and the corrections which must be made for absorption and extinction in order to obtain $|F|$ from intensity may have some uncertainty associated with them. On the one hand, these types of errors may be considered as systematic since their effect on the measurement of a structure factor from the individual crystal will always be the same. On the other hand, if we repeat the measurement on many crystals, such errors might well prove to be unbiased, that is, not systematic. The definition of systematic error thus depends on what we mean by a repetition of the experiment. Do we mean measurement of the same member of an $\{hkl\}$ form on one crystal on the same instrument? Or do we mean that one or more of these factors may be changed? By changing any experimental variable, we change the population of possible ΔF's and hence the bias $\mathscr{S}$ and variance $\sigma^2(\Delta F)$.

In practice it seems that a good working definition of systematic error would be that bias which remains when all controllable experimental factors are kept fixed.

It should be the goal of any intensity measurement project such as those sponsored by the ACA (Abrahams, Alexander, Furnas, Hamilton, Ladell, Okaya, Young & Zalkin, 1967) and the IUCr Commission on Crystallographic Apparatus (Abrahams, Hamilton & Mathieson, 1969) to attempt to estimate $\mathscr{S}$ and $\sigma^2(\Delta F)$ for the experimental techniques in use. In a more limited way, we will attempt in this paper to determine what assumptions are required in order to obtain useful estimates of these quantities by a comparison of X-ray and neutron diffraction data.

Errors in the model

In the previous section, we have discussed the nature of experimental error – error that prevents us from obtaining exact values of the structure factor magnitudes. In this section, some further discussion of what we have called theoretical error – error in the model – is presented. The results of a crystallographic study are almost always presented in terms of numerical values for the parameters which are used to particularize a general model; these are typically mean atomic position parameters and parameters describing the thermal motion.

Although at first sight direct use of the Fourier method would not seem to require a model, the scattering density synthesis does depend on the phases calculated from a model, and features derived from scattering density maps thus depend on the parameters of the assumed model. The only exception to this statement would possibly be the case of simple, centrosymmetric structures, where the signs do not depend on small departures of the structure from the assumed model. Since such structures are, however, usually examined with a view toward exploring subtleties of the scattering density, the changes in sign of a few weak reflections due to errors in the model might nevertheless cause sufficient perturbation of the calculated scattering density to obscure the features of interest (see, *e.g.* Dawson, 1967).

In X-ray diffraction work, the model usually includes the assumption that the atomic scattering amplitudes $f_i(\mathbf{h})$ are those calculated from the free atom wave functions. This assumption can be shown to lead to errors in the atomic positional parameters (see *e.g.* Coppens & Coulson, 1967) and, more severely, in the thermal motion parameters. In this meeting, several papers have discussed the efforts being made to break away from this assumption. It is clear however from the form of (2) that $f_i(\mathbf{h})$ and $T_i(\mathbf{h})$ cannot be separately determined by X-rays, nor in fact is $\mathbf{r}_i$ measureable independently of $T_i(\mathbf{h})$ and $f_i(\mathbf{h})$, and that one must be guided by theory or by results from other structural methods.

It is in this area that neutron diffraction can be useful, for in neutron diffraction $f_i(\mathbf{h})$ is constant for any given nucleus. If we can determine $T_i(\mathbf{h})$ and $\mathbf{r}_i$ in a neutron diffraction experiment, we may assume that these are also valid for the X-ray experiment and it remains to determine $f_i(\mathbf{h})$ from the X-ray data; this may be done either by Fourier methods (see *e.g.* Coppens, 1967, 1968) or by refinement of parameters in a model for $f_i(\mathbf{h})$ (see *e.g.* Stewart, 1968).

It is also clear from these considerations that if $T_i(\mathbf{h})$ is to be determined independently of any assumptions concerning $f_i(\mathbf{h})$, neutron diffraction is the preferred method. Whether this is an important qualification depends of course on the magnitude of the uncertainty in the X-ray $f_i(\mathbf{h})$ and in the desired accuracy of $T_i(\mathbf{h})$. It is my opinion that many problems in molecular dynamics may be solved to a sufficient degree of accuracy by X-ray diffraction even under the assumption of free-atom scattering factors; this point will be demonstrated by some numerical examples in the final section of this paper.

In both neutron and X-ray diffraction, parameters for $T_i(\mathbf{h})$ are usually refined on the basis of an assumption of harmonic motion for all atoms; this leads to a three-dimensional normal probability density function as the form for $T_i(\mathbf{h})$. It is clear from many experimental measurements that this is not a valid assumption for most solids, although it is again true that it is valid to an interesting degree of approximation. Some interesting and successful attempts to refine non-harmonic thermal parameters have been made (Dawson, 1967, 1969; Willis, 1965), and an elegant general treatment has been given by Johnson (1969).

It is quite proper to refine parameters in an incomplete or incorrect model, provided that one realizes and clearly states that the model may be inadequate. If the harmonic approximation is used for the thermal parameters, one may state that a harmonic approximation has been used and that the quoted parameters are the best parameters under the assumptions of this approximation. If more sophisticated models of thermal motion are then adopted, a different set of parameters may be obtained. Furthermore, any additional parameters obtained may not be orthogonal to the old parameters, and the values of the old parameters may consequently change – many times their estimated standard deviations under the assumptions of the incorrect model. It is very important to note that the estimated atomic positions $\mathbf{r}_i$ may depend strongly on the parameters for thermal motion, so that errors in the model for $T_i(\mathbf{h})$ may cause errors in the $\mathbf{r}_i$ – again many times their estimated standard deviations. (Johnson (1969) has analyzed this aspect of the problem in terms of the cumulants of the probability distribution function for the atomic positions.)

Systematic error in the derived parameters

If there is systematic error or bias in the measurement of the structure factors, it is appropriate to examine the effect of this in producing a bias in the derived positional and thermal parameters. A useful general statement cannot be made, but the following considerations are important. In the usual least-squares procedure for the refinement of crystal structures, we estimate the shifts in the parameters by the following equations (see *e.g.* Hamilton, 1964, p. 124 ff.):

$$\Delta\bar{\mathbf{X}} = \mathbf{B}^{-1}\mathbf{A}'\mathbf{P}\Delta\mathbf{F}\,, \tag{8}$$

where $\mathbf{B}$ is the normal equation matrix, $\mathbf{A}$ is the design matrix, $\mathbf{P}$ is a weight matrix, and $\Delta\mathbf{F}$ is composed of $\mathbf{F}_{\text{obs}} - \mathbf{F}_{\text{calc}}$. If there is bias or systematic error in any of the ΔF's, the bias in any derived parameter $\Delta\bar{X}$ may be calculated by use of (8) at the conclusion of the refinement when the elements of all the matrices are known. In general then, bias or systematic error in the measurements will result in bias or systematic error in the derived parameters. There are some special cases where this will not be entirely true; that is, some of the parameters may be biased and others may not. The most common example is our complete lack of knowledge concerning the scale factor in a diffraction experiment. If we think we are measuring absolute values of the structure factors but are actually in error by a multiplicative factor, there will be bias in each of the measurements. Nevertheless, we do not expect this to affect the positional parameters or the shapes of the thermal ellipsoids; it will however introduce a large bias into the determination of the overall mean temperature factor. A similar argument may be made for systematic errors in the observations which are monotonically decreasing functions of sin θ/λ. Again a large bias will appear in the thermal parameters but not necessarily so in the positional parameters. In particular cases, the effect of various types of systematic error may be examined by use of equation (8). Such an approach has been used by Abrahams (1969).

In any case where systematic error in the observations may result in systematic error in the refined parameters, the refinement will lead to unrealistically low values of the agreement factors commonly quoted and of the estimated standard deviations. These are measures of the ability of the model to fit the data, and if parameters of the model are correlated with errors in the observations, biased values of the parameters can create a good fit to the observations even though the accuracy (agreement between refined and 'true' parameter values) is low.

Measures of discrepancy between two experiments

In the final sections of this paper, we would like to compare the results of neutron and X-ray diffraction experiments on the same compounds. There are two useful methods of approach that we will use in this section. One of these involves an application of the well-known χ^2 test to the sum of the weighted differences between the two experiments; the other is a method for the simultaneous examination of any number of independent unrestricted hypotheses (Scheffé, 1953; see also Hamilton, 1964, pp. 117–122).

Consider a crystal structure problem in which we have carried out two experiments, each to determine N parameters, one by neutron diffraction and one by X-ray diffraction. These experiments have resulted in the estimated parameters

$$\begin{array}{ll} \text{Neutron:} & \{p_i^{\mathrm{N}}:\ i=1, N\} \\ \text{X-ray:} & \{p_i^{\mathrm{X}}:\ i=1, N\} \end{array} \tag{9}$$

with estimated standard deviations

$$\begin{array}{ll} \text{Neutron:} & \{\sigma_i^{\mathrm{N}}:\ i=1, \ldots, N\} \\ X\text{-ray:} & \{\sigma_i^{\mathrm{X}}:\ i=1, \ldots, N\}\,. \end{array} \tag{10}$$

The differences between the X-ray and neutron parameters may be defined as

$$\Delta_i = p_i^{\mathrm{X}} - p_i^{\mathrm{N}} \tag{11}$$

and the weighted differences as

$$R_i = \Delta_i / \sigma_i \,, \tag{12}$$

with the standard deviation of the difference defined as

$$\sigma_i = [(\sigma_i^{\mathrm{X}})^2 + (\sigma_i^{\mathrm{N}})^2]^{1/2} \,. \tag{13}$$

We may test the hypothesis that the quantities R_i are drawn from a normal population with unit variance and zero mean by computing the statistical measure

$$R^2 = \sum_{i=1}^{N} R_i^2 \tag{14}$$

as testing as χ^2 with N degrees of freedom.[*] The hypothesis may be rejected with an $\alpha\%$ probability of falsely rejecting a true hypothesis if the calculated value of R^2 exceeds the tabulated value of $\chi^2_{N,\alpha}$.[†] Since we expect the hypothesis to be true if only random error is present, we may conclude that there are some systematic differences between the two experiments. This may be for a number of reasons. If the σ's are too small in one or both experiments, we will be required to reject the hypothesis. As noted above, σ's that are too small may result from systematic experimental error of various kinds. Furthermore, there may be real differences between the true values for the two experiments. Another possibility, and the most likely one, is that the wrong model has been refined in one or both of the experiments, *e.g.* a model including spherical scattering factors in the X-ray experiment. The reasons for the differences between the experiments must be obtained from outside the realm of statistics. The statistical test only confirms that there is a high probability of difference; it does not pinpoint the source of this difference.

We may also test subsets of the parameters for significant differences. For any subset of m parameters, we may calculate

$$R^2 = \sum_{i=1}^{m} R_i^2 \tag{15}$$

and test as $\chi^2_{m,\alpha}$. In the examples below, we shall apply tests on partial parameter sets made up of all the β_{11} parameters, *etc.* Systematic observational error and systematic differences in the theoretical model may each be expected to affect the positional and thermal parameters differently.

Significance of individual parameter differences

For the examination of the significance of individual parameter differences, the first temptation is to use Student's t test. If the parameter estimates have been based on M degrees of freedom, the statistic

$$R_i = \Delta_i / \sigma_i \tag{16}$$

may be tested as Student's t with M degrees of freedom at some significance level α. If M is large, as it will usually be in accurate work, percentage points of the normal distribution may be used instead. A confidence interval on the true value R_i^0 may be defined as follows

$$P(R_i - t_{M,\alpha} < R_i^0 < R_i + t_{M,\alpha}) = 1 - \alpha \,. \tag{17}$$

Another way of stating this is that the hypothesis

$$R_i^0 = 0 \tag{18}$$

may be rejected if $|R_i|$ exceeds $t_{M,\alpha}$. The probability of rejection of a true hypothesis is then α.

Now if we are examining a set of 100 parameters with mean value zero, we may expect $100\,\alpha$ of them to exceed $t_{M,\alpha}$. For $M = \infty$ and $\alpha = 0{\cdot}05$, the value of t is just the 0·05 percentage point of the normal distribution: 1·96. We may thus expect that for five parameters out of a hundred the Studentized difference R_i will have a magnitude exceeding 1·96. It would be incorrect to select these parameters as being statistically different from zero. The t test must be based on a single *a priori* hypothesis. One cannot simply take the largest deviation and say that it is significant. This point should be clear to all crystallographers, but one all too often finds a description of a structure determination in which one bond length out of fifty differs from its chemically expected value by a few times the estimated σ, and elaborate theories are built to explain the difference. Such a procedure is of course incorrect.

There are several methods which can be used to test multiple hypotheses or set up multiple confidence limits. The choice depends somewhat on the type of risk that one is willing to make in making an incorrect statement. One method has been described by Scheffé (1953) (see also Hamilton, 1964, page 117). In the present context we may apply this in the following way. If N parameters have been refined, we may combine these in any possible linear combinations:

$$\left.\begin{aligned} y_i &= \sum_{i=1}^{N} a_i x_i \\ \sigma^2(y_i) &= \sum_{i=1}^{N} a_i^2 \sigma^2(x_i) \,. \end{aligned}\right\} \tag{19}$$

---

[*] In general, we should calculate the statistical measure

$$R^2 = \mathbf{\Delta}'(\mathbf{M}_{\mathrm{N}} + \mathbf{M}_{\mathrm{X}})^{-1}\mathbf{\Delta}$$

where $\mathbf{M}_{\mathrm{N}}$ and $\mathbf{M}_{\mathrm{X}}$ are the variance-covariance matrices for the neutron and X-ray experiments respectively. $\mathbf{\Delta}$ is a column matrix of the Δ_i's.

[†] We assume here that the parameter estimates for both experiments are carried out with data sets with many more observations than variables, *i.e.* the numbers of degrees of freedom for the estimates of the σ's are large. If this is not true, one should use a variance ratio F rather than χ^2, but this makes no essential difference in the arguments. Certainly for precise crystal structure work, when the differences between two experiments are to be examined, the number of degrees of freedom should be large enough (more than a few hundred) so that χ^2 may be used with little error.

Simultaneous confidence limits may be set up as follows; we may say that each true value y_i^0 satisfies the following inequality

$$y_i - S\sigma(y_i) < y_i^0 < y_i + S\sigma(y_i) \quad (20)$$

where S is defined by

$$S^2 = \chi^2{}_{N,\alpha} . \quad (21)$$

If we adopt this criterion and carry out many such experiments, we should expect that in $100(1-\alpha)$ per cent of the experiments all the statements will be correct, while in 100 α per cent of the experiments, one or more statements may be incorrect. As the examples below show, such an approach results in very broad confidence intervals; the results may be unsatisfying to those who are looking for subtle effects. The width of the confidence intervals is large because of the fact that we admit hypotheses suggested by the data.

If there are specific effects being sought, or if the experiment has been carried out to test particular hypotheses, one may be justified in going back to the usual t test – or an F test in the case of a multi-dimensional hypothesis (Hamilton, 1964, page 139). Such a test could be used for example to test the following hypothesis: all the differences in the m thermal parameters are zero. Testing this as $F_{m,\infty,\alpha}$ is identical to the χ^2 test on the thermal parameters. And indeed separating out individual parameters or groups of parameters to be tested as χ^2 suffers from the same criticism as that which may be directed at simultaneous t tests. The hypotheses must be *a priori* hypotheses and not selected on the basis of the results of the experiment.

Some results

There are few structures which have been accurately examined by both neutron and X-ray diffraction with modern diffractometer techniques. We will summarize the results for some of these here; the results for heavy atoms and hydrogen atoms will be tabulated separately except in the case of *s*-triazine. Table 1 gives some pertinent details of the refinements. The hydrogen atom thermal parameters were not refined in the analysis of the X-ray data for potassium hydrogen diaspirinate; none of the hydrogen atom parameters were refined for the Holly Springs hydroxyapatite. The methylglyoxal bisguanylhydrazone X-ray data were based on visually estimated photographic intensities.

For all parameters for which values were available from both the X-ray and neutron analysis, the difference Δ_i, the weighted difference R_i, and its variance σ_i^2 as defined in (12) and (13) were calculated and tabulated. R^2 was then calculated by (15) for each of the following sets of parameters: x for all atoms, y for all atoms, z for all atoms, each β_{ij} for all atoms, all thermal parameters, all positional parameters, and all parameters. These values are tabulated in Table 2, where they are compared with significant values of χ^2 at the 0·05 significance level. The details of the comparisons will be discussed in the next section with reference to individual compounds. We note here that the calculated values of R^2 are generally significant for both positional and thermal parameters and for both heavy and hydrogen atoms.* Furthermore, the significance of the differences for the hydrogen atom positional parameters is much greater than that for the heavy atoms. Even if the significance of the difference for the heavy atoms is due to systematic error in one or both experiments (a very likely possibility), there seems to be no question but that a very real effect is being seen in the hydrogen atom positions. Curiously enough, the differences in the thermal parameters appear to be more significant for the heavy atoms than for the hydrogen atoms, although they are highly significant in both cases.

Although we do not wish to repeat all the parameter values and their differences here it does seem useful to report in Table 3 the largest values of $|R_i|$ obtained for each parameter type and each experiment. In addition to these individual contrasts, we have also calculated ratios

$$y_i/\sigma(y_i) \quad (22)$$

for the following weighted mean parameter differences

$$y_i = \sum_{i=1}^{n} \omega_i x_i \Big/ \sum_{i=1}^{n} \omega_i , \quad (23)$$

where the sum is over the n atoms present in the structure and where x_i may be Δx, Δy, Δz, or any of the $\Delta\beta_{ij}$. We have finally calculated the weighted mean difference of all positional parameters and of all thermal parameters. These values (22) are also presented in Table 3 as 'mean Δ/σ'.

Each of the numbers in Table 3 could be tested in a separate t test, and on this basis many of them would be individually significant. A more conservative approach† is to establish confidence limits as suggested by (20) and (21) and the appropriate values of S are also given in the table. Only a few of the individual parameter differences and other contrasts would be deemed significantly non-zero on this basis. More interesting contrasts could be made between bond lengths and other derived parameters. It seems likely that the differences would be of greater significance than the mean positional parameters reported in the lower part of Table 3. Before we discuss individual compounds, it is further worthy of note that for all but one of the diffractometer experiments mean diagonal elements of

---

* With the exception of deuterated oxalic acid, the significance of differences in heavy atom positions is marginal and (in the absence of chemical information) it is questionable whether much should be made of it except as an indication that the quoted σ's are probably somewhat too small in every experiment referred to here.

† This approach is probably too conservative. If we are guided by chemical reasoning, our hypotheses will usually be *a priori* and *not* suggested by the data.

Table 1. *Some structures which have been refined byX-ray and neutron diffraction*

Potassium hydrogen diaspirinate	(KHDA)	X-ray	Manojlovic & Speakman (1967)
		Neutron	Sequeira, Berkebile & Hamilton (1968)
Oxalic acid dihydrate, α phase	(α-POX)	X-ray	Delaplane & Ibers (1968)
		Neutron	Cox, Sabine & Craven (1968)
Oxalic acid dihydrate, α phase (completely deuterated)	(α-DOX)	X-ray	Delaplane & Ibers (1968)
		Neutron	Coppens & Sabine (1968)
Holly Springs hydroxyapatite	(HSHA)	X-ray	Sudarsanan & Young (1967)
		Neutron	
s-Triazine	(STZ)	X-ray	Coppens (1967)
		Neutron	
Methylglyoxal bisguanylhydrazone	(GAG)	X-ray	Hamilton & La Placa (1968)
		Neutron	

		KHDA		α-POX		α-DOX		HSHA		STZ		GAG	
		X-ray	Neutron	X-ray	Neutron	X-ray	Neutron	X-ray	Neutron	X-ray	Neutron	X-ray	Neutron
Number of observations		2731	1622	547	661	555	935	500	253	162	83	869	722
Number of structural parameters		151	191	63	63	63	63	39	42	15	15	191	287
Number of heavy atoms refined		14	14	4	4	4	4	7	7	2	2	16	16
Number of hydrogen atoms refined		8	8	3	3	3	3	0	1	1	1	16	16
R†		0·099	0·052	0·028	0·072	0·028	0·043	0·029	0·028	0·050	0·073	0·029	0·072
wR		0·122	0·079	0·039	0·092	0·039	0·044	0·028	0·025	0·039	0·053	0·080	0·073
Typical values (Å)	$\sigma(x)$ heavy	0·003	0·003	0·001	0·002	0·001	0·002	0·002	0·002	0·003	0·006	0·010	0·010
	$\sigma(x)$ hydrogen	0·050*	0·005*	0·015	0·005	0·015	0·002	—	0·004	0·040	0·013	0·150	0·020
	$\sigma(U^{1/2})$ heavy	0·004	0·005	0·002	0·003	0·002	0·002	0·004	0·004	0·005	0·005	0·015	0·015
	$\sigma(U^{1/2})$ hydrogen	—	0·005	0·025	0·004	0·030	0·002	—	0·008	0·080	0·020	—	0·020

* For hydrogen atoms in methyl group, about 6 times as large (10%).

† $R = \dfrac{\Sigma\,||F_o|-|F_c||}{\Sigma\,|F_o|}$ $\qquad wR = \left[\dfrac{\Sigma\, w||F_o|-|F_c||^2}{\Sigma\, w|F_o|^2}\right]^{1/2}$.

Table 2. χ^2 *test on parameter types*

Significant values at the 0·05 level are given in italics.

Compound	KHDA heavy	KHDA hyd	α-POX heavy	α-POX hyd	α-DOX heavy	α-DOX light	HSHA	*s*-Triazine	GAG heavy	GAG hydrogen
x	19, *22*	33, *14*	3, *9*	119, *8*	9, *9*	143, *8*	10, *11*	13, *8*	30, *26*	40, *26*
y	26, *24*	13, *14*	5, *9*	46, *8*	4, *9*	58, *8*	7, *11*	— —	37, *26*	58, *26*
z	22, *22*	44, *14*	11, *9*	100, *8*	31, *9*	110, *8*	8, *8*	— —	43, *25*	37, *26*
β_{11}	29, *24*	— —	11, *9*	9, *8*	86, *9*	22, *8*	15, *14*	5, *8*	23, *26*	— —
β_{22}	29, *24*	— —	249, *9*	19, *8*	153, *9*	16, *8*	19, *11*	31, *8*	37, *26*	— —
β_{33}	471, *24*	— —	374, *9*	24, *8*	89, *9*	14, *8*	46, *14*	14, *8*	33, *26*	— —
β_{12}	11, *22*	— —	109, *9*	3, *8*	67, *9*	5, *8*	3, *11*	— —	31, *26*	— —
β_{13}	113, *24*	— —	47, *9*	39, *8*	38, *9*	49, *8*	8, *4*	8, *8*	17, *26*	— —
β_{23}	9, *22*	— —	4, *9*	13, *8*	10, *9*	17, *8*	3, *4*	— —	37, *26*	— —
All position	67, *56*	90, *33*	18, *21*	265, *17*	44, *21*	311, *17*	25, 22	13, *8*	111, *64*	135, *65*
All thermal	662, *104*	— —	793, *36*	105, *29*	442, *36*	124, *29*	94, *39*	57, *21*	178, *120*	— —
All parameter	729, *144*	90, *33*	811, *51*	370, *40*	486, *51*	435, *40*	119, *54*	70, *25*	289, *173*	135, *65*

the thermal vibrational tensor are larger for X-rays than for neutrons. In each structure, there are however some individual exceptions.

Comments on the individual structures

Potassium hydrogen diaspirinate

From Table 2, we see that the χ^2 test reveals highly significant discrepancies for β_{33} and β_{13}. This is confirmed by the numbers in Table 3, where the mean β_{33} is highly significant even on the basis of the conservative S test. The X-ray β_{33} was larger by about 30–50% for each of the heavy atoms. This corresponds to a difference of about 0·05 Å in the r.m.s. amplitude in this direction, a difference of 20%. The other r.m.s. amplitudes agree to about 5% or less. There is no obvious structural reason why this discrepancy should exist; we conclude that the discrepancy is due to some systematic error in either the X-ray or the neutron experiment. The magnitude of the difference is larger than would be expected from improper treatment of bonding effects. It should be noted that the X-ray data were not corrected for absorption – a necessity when subtle effects are sought. For the hydrogen atoms, Table 1 indicates that the weighted discrepancies are larger than for the heavy atoms. The differences are largely confined to a plane perpendicular to the y axis. Anisotropic thermal parameters were not refined for hydrogen in the X-ray study.

Oxalic acid dihydrate

There do not seem to be significant differences in heavy atom parameters except for the z parameter of atom 2 in the deuterated material. The difference is only 0·008 Å; the significance arises from the very small standard deviations* obtained from the refinements. This is of the order of magnitude of position shifts possible from bonding effects,† but it is also possible that this is one of these cases where errors have piled up in the coordinate of one atom and that there is no physical significance. There are very significant differences in most of the heavy atom thermal parameters. Coppens & Sabine (1969) have interpreted these in terms of inadequacies in the X-ray scattering factors. The differences are small on an absolute basis – a maximum of about 0·02 Å or 10% in the r.m.s. amplitudes. It is clear that work of the highest quality, absolutely free of serious systematic error, is necessary to reveal these differences. There is no doubt of the statistical significance here; the S test (Table 3) gives significant differences for a few of the thermal parameters and more impressively indicates that the mean thermal parameters are significantly greater in the X-ray case. The implications of these facts have been

---

* It should be noted that the standard deviations used in most of these calculations were available to only one significant figure.

† The effect is in the same direction in the proton-containing material.

explored by Coppens (1969) in another paper delivered at this conference.

The analysis for the hydrogen atoms in both the normal and the deuterated samples indicates significant differences. The χ^2 test on the positional parameters is unambiguous. The individual contrasts are also on the edge of significance by the conservative S test at the 0·05 significance level. Most remarkable are the comparison between the positional parameters for the protonated and the deuterated samples. Table 4 illustrates the remarkable agreement between the differences and provides the best evidence available to date for a systematic difference between X-ray and neutron parameters that must be reproduced by some theoretical model. The practically identical shifts in apparent position in the hydrogen and deuterium compounds must clearly be understood in terms of electron density shifts in the O–H bonds.

The shifts in the thermal parameters also show a reasonable consistency between the protonated and deuterated compounds and speak well for the meaningfulness of all four parameter sets.

Holly Springs hydroxyapatite

Again the χ^2 test reveals significant differences in both positional and thermal parameters, although the effects are less dramatic than in the two other compounds discussed above. There is again better agreement among the positional parameters than among the thermal parameters. None of the individual deviations are significant by the S test. Again the mean thermal parameters are somewhat larger in the X-ray study.

s-Triazine

In this very simple structure, there are significant differences in both positional and thermal parameters. Examination of the individual position parameters (not tabulated) by the χ^2 test does not allow one to reject the hypothesis that the heavy atom parameters are equal. There is a large deviation (2·76σ) for the hydrogen atom positional parameter. The deviations in β_{22} are large for each atom. Although they are not significantly large by the S test, Coppens (1967) has shown that the differences are such as to be in agreement with preconceived notions regarding electron density distributions (Coppens & Coulson, 1967).

Methylglyoxal bisguanylhydrazone

These results are included partially because they represent a level of precision in parameter determination that is somewhat worse than most of the other experiments reported here. The X-ray experiment is the only one reported here for which photographic data were used. The χ^2 test for the heavy atom parameters shows marginally significant differences in each case. Since the standard deviations here are larger than expected bonding effects, the most reasonable conclusion is that there are systematic errors in one or both experiments that have caused the estimated σ's to be too small by a factor of 1·5–2·0. The largest discrepancy for a heavy atom parameter was surprisingly for one of the Cl positional parameters. Although anomalous dispersion was correctly treated in the least-squares refinement of this acentric structure, it is possible that uncertainty in the value of the anomalous scattering parameter has

Table 3. (*a*) *Extreme values of* $|\Delta/\sigma|$, *and* (*b*) *weighted mean* Δ/σ, *for each parameter type*

Compound	KHDA Heavy	KHDA Hydrogen	α-POX Heavy	α-POX Hydrogen	α-DOX Heavy	α-DOX Hydrogen	HSHA	STZ	GAG Heavy	GAG Hydrogen
(*a*) Extreme values of $\lvert\Delta/\sigma\rvert$										
x	2·1	4·9	1·3	8·4	2·2	8·2	2·2	2·8	3·0	3·3
y	2·4	1·2	2·1	5·9	1·2	6·3	2·1	–	2·6	6·0
z	2·4	4·7	3·1	8·2	5·0	8·7	2·7	–	5·4	2·9
β_{11}	2·3	–	2·7	2·9	6·8	4·7	2·1	2·1	2·3	–
β_{22}	2·8	–	9·3	3·3	6·8	2·9	2·8	5·2	2·4	–
β_{33}	10·8	–	12·0	3·7	5·7	2·6	4·5	1·8	2·8	–
β_{12}	2·3	–	9·2	1·1	7·8	1·6	1·4	–	2·6	–
β_{13}	5·7	–	5·8	4·8	5·0	5·4	2·8	2·7	2·5	–
β_{23}	1·9	–	1·7	3·1	2·5	3·7	2·1	–	2·8	–
(*b*) Weighted mean Δ/σ										
x	+0·4	−1·2	−1·3	+2·1	−1·1	−11·1	0·8	−2·5	−1·0	0·2
y	−0·8	−0·5	+0·6	−4·8	−0·2	−5·7	2·1	–	+2·0	+3·6
z	+1·6	+0·8	−0·5	−1·8	−2·1	+5·9	0·3	–	−5·5	−1·1
β_{11}	−3·5	–	+2·8	+1·1	8·8	1·9	0·4	1·8	+0·7	–
β_{22}	−2·0	–	+15·4	+3·7	12·2	3·3	0·2	2·1	−1·0	–
β_{33}	+21·0	–	+18·7	+4·3	9·2	3·3	4·1	3·1	+2·8	–
β_{12}	−0·3	–	−5·7	0·5	−3·3	0·7	0·1	–	−0·9	–
β_{13}	+9·7	–	+5·1	−4·4	4·9	−5·0	−2·8	0·3	+0·5	–
β_{23}	−0·5	–	+0·6	2·1	3·0	1·0	−1·8	–	−1·3	–
Mean position	0·7	−0·9	−2·3	−1·7	−0·9	−2·6	2·0	−2·5	−1·0	2·3
Mean thermal	10·1	–	12·1	2·2	17·4	1·0	1·2	3·5	−0·0	–
$S_{0\cdot05}$	12	6	7	7	7	7	7	5	13	8
D.F.*	122	21	36	27	36	27	39	15	143	48

* The number of degrees of freedom was taken to be the number of parameters refined by both X-ray and neutron diffraction for each column.

introduced bias into the determination of the Cl parameters. This tentative conclusion suggests that a combination of neutron and X-ray scattering data may be fruitful in the quantitative investigation of anomalous scattering factors, much as it has in the investigation of electron density distributions.

At the level of precision of these two data sets, the differences in hydrogen position are no more significant than those in heavy atom positions. The hydrogen temperature factors were not refined by X-rays.

Conclusions regarding the present comparisons

In each of the cases discussed here, there are significant differences between the neutron and X-ray diffraction determined parameters. As discussed in the earlier sections of this paper, this significance may be due to systematic errors in the data or to errors in the model on which the parameters are refined. The IUCr single crystal intensity project report part II (Abrahams & Hamilton, 1969) suggests that systematic errors in diffraction experiments as performed today may often cause estimated standard deviations from least-squares refinements to be too small by a factor of two if the suggested factor of two is characteristic of the experiments reported here. The significance of the differences between X-ray and neutron-diffraction determined positional parameters for heavy atoms is thus marginal. The differences in hydrogen atom positions are quite real, as the consistency of the oxalic acid results testifies.

There are large differences in apparent thermal parameters. In general, X-ray thermal parameters appear to be significantly larger than neutron thermal parameters for heavy atoms; this reflects the inadequacy of the free-atom approximation for the X-ray scattering factors as discussed in detail by Coppens (1968, 1969). There are also differences in hydrogen thermal parameters, but these are intimately bound up with the bias in the positional parameters arising from an inadequate description of the electron density associated with a vibrating hydrogen atom. A number of people have suggested using the neutron-diffraction determined parameters to attempt to refine better models for the X-ray scattering. This would seem to be especially appropriate for hydrogen atoms, where the differences are large. It is encouraging that modern X-ray diffraction techniques are capable of determining apparent hydrogen atom positions to a precision of 0·02 Å. Much of interest can be learned from an analysis of these experimental results. For the accurate investigation of bonding effects involving heavy atoms, where the differences are considerably smaller, it would seem necessary to have experimental data an order of magnitude more accurate than most of those presently available. Such improvement will be difficult but is within the realm of possibility.

In all of this type of work, it is essential that theory be a guide to experiment. Hypotheses must be phrased and experiments carried out to test them. *A postiori* hypotheses are fraught with danger. Whenever possible, it is desirable to carry out important experiments more than once with some large experimental factors changed, *e.g.* exchange of H for D (although this introduces its own complication in the dynamical interpretation), repetition of the experiment on a different crystal in a different diffractometer geometry – perhaps with a crystal grown under different conditions. Hope-

Table 4. *Oxalic acid dihydrate hydrogen atoms positional parameters*

Values for deuterated compound are in italics

	X-ray	Neutron	Δ	$\sigma(\Delta)$	Ratio
x_1	0·0357	0·0293	0·0064	0·0021	3·020
	0·0368	*0·0259*	*0·0109*	*0·0020*	*5·423*
y_1	0·9953	1·0093	−0·0140	0·0045	−3·136
	0·9894	*1·0079*	*−0·0185*	*0·0044*	*−4·187*
z_1	0·2087	0·2189	−0·0102	0·0012	−8·246
	0·2057	*0·2171*	*−0·0114*	*0·0013*	*−8·743*
x_2	0·0588	0·0740	−0·0152	0·0024	−6·322
	0·0554	*0·0712*	*−0·0158*	*0·0023*	*−6·844*
y_2	0·1587	0·1864	−0·0277	0·0047	−5·914
	0·1564	*0·1849*	*−0·0285*	*0·0045*	*−6·295*
z_2	0·3795	0·3858	−0·0063	0·0016	−3·870
	0·3787	*0·3849*	*−0·0062*	*0·0016*	*−3·867*
x_3	−0·3869	−0·3599	−0·0270	0·0032	−8·364
	−0·3878	*−0·3591*	*−0·0287*	*0·0035*	*−8·170*
y_3	0·4508	0·4447	0·0061	0·0053	1·153
	0·4510	*0·4453*	*0·0057*	*0·0051*	*1·112*
z_3	0·1584	0·1508	0·0076	0·0018	4·122
	0·1604	*0·1522*	*0·0082*	*0·0019*	*4·310*

fully, one of the results of this conference will be to make all of us more aware of the types and magnitudes of error that can be present in diffractometric experiments and of the methods for recognizing and correcting for such systematic errors that do occur.

Accuracy today

How well are we doing today in the measurement of positional and thermal parameters by diffraction techniques? What can be done to improve this situation? These are the questions we face today.

The internal precision of the experiments reported here – some of which appear to be among the best available – suggests the following:

(*a*) Heavy atom coordinates can be determined to a precision of 0·001–0·002 Å by both neutron and X-ray diffraction.

(*b*) Hydrogen atom coordinates can be determined to a precision of 0·001–0·002 Å by neutron diffraction and 0·01–0·02 by X-ray diffraction.

(*c*) Root-mean-square amplitudes of vibration may be determined to a precision of 0·001–0·002 Å. This is about 1% of usual r.m.s. amplitudes for rigid or hydrogen-bonded organic molecules at room temperature. The accuracy in X-ray diffraction is comparable to that in neutron diffraction for heavy atoms; again hydrogen atom parameters are less precise by an order of magnitude.

If the differences between the neutron and X-ray experiments discussed here are due to systematic experimental error rather than imperfections in the model (a possibility which we consider to be unlikely), this systematic error would seem on the average to amount to about three times the estimated σ's from the least-squares refinements. We thus suggest that the *maximum* amount of systematic error remaining in the best diffraction experiments may cause uncertainties of 0·006 Å in atomic distances and 0·006 Å in r.m.s. amplitudes of vibration. Further carefully designed inter-experiment comparisons such as that attempted in the single crystal intensity projects (Abrahams, Hamilton & Mathieson, 1969; Abrahams *et al.*, 1967; Mathieson, 1969) will be necessary to get a thorough understanding of the types and magnitudes of systematic error that may affect diffractometer experiments. We emphasize that accuracies such as those suggested in the present section are only possible if the utmost care is taken as to diffractometer alignment, spectral purity, crystal quality, absorption and extinction corrections, and proper error-free least-squares refinements.

One sidelight of these comparisons is the conclusion that X-ray diffraction work is adequate for the study of most structural problems. Neutron diffraction is required only when results of the greatest accuracy are needed regarding hydrogen atom positions and thermal vibrational amplitudes. The determination of hydrogen atom positions to 0·02 Å by X-rays, a feat possible today, should adequately serve the needs of the chemical crystallographer. Even in the determination of vibrational amplitudes of heavy atoms, where it is realized that bonding effects may cause some systematic discrepancies in the amplitudes obtained, the X-ray data should suffice for most studies in molecular dynamics. Bonding effects rarely account for more than 10 per cent error in the r.m.s. amplitudes. In the next few years, we should see more adequate descriptions of bonded atoms used in structure factor calculations. When this prediction is fulfilled, the agreement between the two methods should be even better than it is today.

The author would like to express his appreciation to his colleagues for communicating their results to him prior to publication.

References

ABRAHAMS, S. C., ALEXANDER, L. E., FURNAS, T. C., HAMILTON, W. C., LADELL, J., OKAYA, Y., YOUNG, R. A. & ZALKIN, A. (1967). *Acta Cryst.* **22**, 1.
ABRAHAMS, S. C. (1969). A**25** 165.
ABRAHAMS, S. C. & HAMILTON, W. C. (1969). *Acta Cryst.* To be published.
ABRAHAMS, S. C., HAMILTON, W. C. & MATHIESON, A. McL. (1969). *Acta Cryst.* To be published.
COPPENS, P. (1967). *Science*, **158**, 1577.
COPPENS, P. (1968). Abstracts ACA meeting, Tucson, Arizona, February 1968.
COPPENS, P. (1969). *Acta Cryst.* A**25**, 180.
COPPENS, P. & COULSON, C. A. (1967). *Acta Cryst.* **23**, 18.
COPPENS, P. & SABINE, T. M. (1968). To be published.
COX, G. W., SABINE, T. & CRAVEN, B. C. (1968). To be published.
DAWSON, B. (1967). *Proc. Roy. Soc.* A**298**, 255. *et. al.*
DAWSON, B. (1969). *Acta Cryst.* A**25**, 12.
DELAPLANE, R. & IBERS, J. A. (1968). To be published.
HAMILTON, W. C. (1964). *Statistics in Physical Science.* New York: The Ronald Press.
HAMILTON, W. C. & LA PLACA, S. J. (1968). *Acta Cryst.* B**24**, 1147.
JOHNSON, C. K. (1969). *Acta Cryst.* A**25**, 187.
MANOJLOVIC, L. & SPEAKMAN, J. C. (1967). *J. Chem. Soc.*, p. 971.
MATHIESON, A. McL. (1969). *Acta Cryst.* A**25**, 264.
SCHEFFÉ, H. (1953). *Biometrika*, **40**, 87.
SEQUEIRA, A., BERKEBILE, C. A. & HAMILTON, W. C. (1967). *J. Mol. Struc.* **1**, 283.
STEWART, R. (1968). *J. Chem. Phys.* In the press.
SUDARSANAN, K. & YOUNG, R. A. (1967). Abstracts ACA Meeting, Minneapolis, Minnesota, August 1967, Paper Q5 and private communication.
WILLIS, B. T. M. (1965). *Acta Cryst.* **18**, 75.

DISCUSSION

MASLEN: Three points arising from the papers of Drs Coppens, Johnson and Hamilton require special emphasis.

(i) The relatively large magnitude of the bonding electron redistribution on scattering factors for molecular crystals containing first row atoms may be established from X-ray evidence alone.

In the electron density distribution obtained by a Fourier synthesis for 1,3,5-triamino-2,4,6-trinitrobenzene (Fig. 1, Cady & Larson, *Acta Cryst.* (1965), **18**, 485) for example, there are large differences in the carbon peak heights which can only be interpreted in terms of a difference in net charge at these positions. The peak heights for the atoms C(1), C(3) and C(5) are all approximately 11·0 e.Å^{-3}, whereas those for C(2), C(4) and C(6) are close to 12·2 e.Å^{-3}. This is consistent with the charge movements expected for this structure, which have been discussed by Cady & Larson.

(ii) The interaction of the thermal parameters with the electron density distribution may have a serious effect on the inter pretation of thermal data from X-ray analyses.

The flat difference densities obtained in X-ray analyses are often indicative only of high interaction between the electron density distribution and the thermal parameters. In the example referred to in the previous paragraph, very little of the charge difference between the carbon atoms appears in the difference density. (Fig. 2, Cady & Larson, *Acta Cryst.* (1965), **18**, 485) but the thermal parameters of C(1), C(3) and C(5) are consistently higher than those of C(2), C(4) and C(6). This appears to indicate the presence of a threefold buckling motion of the ring of appreciable amplitude, which is in serious contradiction with force constants evaluated theoretically or from spectroscopic data. The latter indicate a much lower amplitude for motions of this kind, and it is clear that the discrepancy is an artifact in the X-ray results resulting from the interaction between electron density and thermal motion.

The differences between librational amplitudes deduced from spectroscopic and X-ray data for some of the polycyclic aromatic hydrocarbons have a similar origin. Rigid body libration frequencies deduced from X-ray evidence for anthracene, which have been quoted by Pawley (*Phys. Stat. Sol.* (1967), **20**, 347) show serious discrepancies with Raman spectra data for the two higher frequency modes. According to the theoretical calculations of Roos & Skancke (*Acta Chem. Scand.* (1967) **21**, 233) the inner carbon atoms, which have no hydrogen substituents, are expected to have acquired a net charge of $-0{\cdot}023e$. The outer carbon atoms, each having a single hydrogen substituent, have an electron deficiency corresponding to a charge of $+0{\cdot}015e$. The errors of the thermal parameters resulting from these small charge movements account for the observed discrepancies. This is supported by a recalculation of the frequencies using only the parameters for the outer carbon atoms, which have similar charge distributions. The difference between the spectroscopic and X-ray frequencies then disappears, although with this restricted set of parameters the highest frequency is not well determined.

(iii) The limitations of the harmonic vibrational representation of thermal motion have a serious effect on the analysis of valence electron structures if the nuclear trajectories have appreciable curvature.

The curvilinear trajectories of librational motions produce a characteristic shape of the electron density distribution which is well illustrated by the acetate oxygen in the structure analysis of basic beryllium acetate (Fig. 9, Tulinsky, *Acta Cryst.* (1959) **12**, 626). If the curvature is large this motion is not well described by the harmonic vibrational approximation, which is commonly used for the analysis of thermal motion. This has the well known effect of displacing the atom position, but it also produces characteristic features in the residual density. This is a serious limitation if X-ray data are to be used for the study of bonding electron distributions. If thermal motion and electron density distributions are to be deconvoluted in an X-ray analysis, more reliable theoretical models for both scattering and temperature factors are required.

COPPENS: I can support Maslen's statement on anthracene rigid body motion. Pawley has calculated **T** and **ω** tensors from potential functions for this molecule and comparison with X-ray results shows that the calculated values are lower than the experimental ones.

POST: I would merely make the point that in a published study of $NaNO_3$, we gave a detailed description of the librating behaviour of the oxygen atom. This work was done with Cu radiation. When the data were extended more recently with Mo radiation, the apparent libration effects disappeared. One wonders to what extent the effects observed in other cases are artifacts.

SRINIVASAN: One important factor that has to be taken into account in all these studies is the anomalous dispersion effect. As has been recently demonstrated by Zachariasen in the case of quartz, and by Marezio in the case of $LiAlO_2$ and similar compounds, even oxygen atoms show measur able dispersion components.

Another comment which I would like to make in connexion with electron distribution again pertains to anomalous scattering. We have recently shown (Srinivasan & Chacko, *Curr. Sci.* (*India*) 1967) that once a structure has been solved and accurate values of Bijvoet pairs $F(H)$ and $F(\bar{H})$ are available one could calculate the 'imaginary' component of electron density distribution arising out of the dispersion component $\Delta f''$ by a Fourier analysis. Such a map gives formally the electron distribution of the inner shells of atoms. The method is also likely to be useful in the actual determination of $\Delta f''$ values of atoms by successive Fourier iteration as well as by least-squares methods.

HAMILTON: In a study of dimethyl GAG which contains HCl of crystallization, the structure being acentric, the only significant difference between the X-ray and neutron data showed up in the positional parameters of the chlorine. We took the anomalous dispersion figures from *International Tables* and these do not appear to have been as good as they ought to have been.

LARSON: At Los Alamos we did some work on refining dispersion terms in least-squares analysis in the structure of $K_3Cu(CN)_4$ (Roof, R. B., Larson, A. C. & Cromer, D. T., *Acta Cryst.* **B24**, 269, 1968). I did the calculations with three different form factors and found that the anomalous dispersion terms which came out of the L. S. analysis were very dependent on the form factor used. I conclude that the model used in calculating f'' is less satisfactory than that used in calculating f_0.

MILLEDGE: Concerning **T**, **ω** tensors, it is almost invariably assumed that they are calculated for rigid bodies. Since we know, from spectroscopic data, that there are internal vibrations, this means that, if these are neglected, you have large numbers of negative amplitudes well outside any reasonable standard deviations and so, unless the calculation is tackled correctly, all **T**, **ω** tensor relative values are too high.

JOHNSON: For the segmented body approach to these almost rigid bodies, we find it practically always necessary, for neutron diffraction studies, to do the best to subtract out the effect of internal vibrations as determined from some normal mode analyses. Also we intend now to put the skewness tensor into this type of calculation. It will not tell us any more about correlation of motion between atoms but will give a cleaner separation of libration from translational effects.

ZACHARIASEN: My comments are on anomalous dispersion effects. The real part $\Delta f'$ cannot be disentangled from the form factor curves used; the imaginary part $\Delta f''$ only shows up in acentric crystals when measuring reflexions H and $\bar{H}$. The accuracy which you get from refinement depends on $\Delta f''$ and this, at present, is best derived from empirical anomalous absorption values given. $\Delta f''$ is only as good as these tables, unless you are dealing with very light atoms when other contributions come in, but still, in my opinion, more reliable than Cromer's calculations. It should be realized that the effect of $\Delta f''$ is very appreciable.

I have recently made measurements on KH_2PO_4 with Mo $K\alpha$ radiation. The reflections are of three types:

(i) Those which have no contributions from K or P but only from O, where no dispersion is observed.

(ii) Those where K and P cooperate completely; here the anomalous dispersion term comes in as the sum of the two $\Delta f''$ and amounts to only about 2% because the reflections are very strong.

(iii) Those where K and P are in opposition. Those reflections are very weak and the difference between the two $\Delta f''$ may amount to as much as 20% of the total.

Acta Cryst. (1969). A**25**, 206 G1·1

Instruments and Techniques Required for Accurate Relative Intensities from Powder Specimens

BY P. M. DE WOLFF AND W. H. SAS

Laboratorium voor Technische Naturkunde, Technische Hogeschoole, Lorentzweg 1, *Delft, The Netherlands*

For the purpose of accurate intensity measurements the use of transmission specimens is recommended. Apart from special advantages with respect to certain features *e.g.* surface roughness, they allow the measurement of the orientation distribution over a large range, using off-symmetry azimuth values. Correction for preferred orientation should then be possible, provided a simple texture model – a cylindrico-symmetrical needle-type texture – can be assumed. Some computing schemes for carrying out the elimination of the texture parameters are discussed.

The techniques referred to in the title can be considered from different viewpoints. For instance, one may ask which of the existing routine techniques is most suitable for attaining a high accuracy? Quite generally, the field can be restricted to counter methods – though it is perhaps worth mentioning that, apart from properties of available film, the fundamental reason for this restriction is the unfortunate spectral film sensitivity rather than any foreseeable limit of reproducibility. Between the different counter diffractometers, there is little essential variation. All are based on the Bragg–Brentano principle, so there seems to be no choice left.

One may ask, then, if the requirement of high accuracy would make it desirable to apply techniques not used routinely at present. We think this may be true with regard to (1) transmission-type diffractometry, in particular when used (2) to measure intensities at off-symmetry azimuths of the specimen plane.

(1) Transmission geometry means the use of a thin slab of powder specimen permitting the diffracted beam to emerge from the back. Though proposed originally as a direct consequence of the application of curved monochromators to counter diffractometry, the transmission specimen has independent merits.

In the first place, the surface layers of a transmission-type specimen contribute no more to the diffracted intensity than corresponds to the volume they occupy, whereas in reflexion-type specimens their contribution can be predominant. Here 'surface-layer' means the layer – with a thickness at least of the order of the average particle diameter – which can be suspected to show systematic deviations from the average distribution of crystallite orientation and (in the case of mixtures) of composition.

Secondly, the effect of surface roughness is much less in transmission than in reflexion, because of the much smaller angle between surface normal and X-ray beam. This is important in the investigation of strongly absorbing powders.

The transmission-type specimen has some obvious disadvantages. Depending upon the material under hand, a slab of uniform thickness may be more difficult to fashion than a reflexion specimen, and it will usually require a binding agent and/or a support. Also the transmission geometry is clearly unfavourable for large Bragg angles. In many cases, however, the use of Mo K radiation will yield sufficient information at low to medium angles.