

of chemically-equivalent bonds from mean values, are about 0.03 Å for Br-C and P-C distances, and 0.04 Å for other distances.

Discussion

A perspective drawing of the molecule is shown in Fig. 1, from which it is evident that the structure is (IIIb, $X=\text{Br}$), and hence the adduct formed from tetraphenylphosphine imide is (IIIb, $X=\text{H}$). The general shape of the molecule is also clear from Fig. 1. A detailed description of the disposition of the various phenyl and methoxycarbonyl groups is probably not very useful since the conformation of the molecule will be determined at least to some extent by intermolecular forces; any information required can readily be derived from Table 2.

The bond distances and valency angles in the molecule (Table 3) are all normal. The phosphorus-phenyl bonds average 1.83 Å ($\sigma \sim 0.025$ Å), not significantly different from the P-C single-bond distance of 1.87 ± 0.02 Å in trimethylphosphine and 1.84 ± 0.02 Å in $[(\text{CH}_3)_2\text{P}\cdot\text{BH}_2]_3$ (Tables of Interatomic Distances, 1958). The P=C length is 1.70 Å. This double-bond distance does not appear to have been measured previously; the reduction below the single-bond length is a little greater than the difference between the single-bond and double-bond covalent radii of phosphorus (Pauling, 1960). The angles at the phosphorus atom are all fairly close to the tetra-

hedral value (mean value 109.4°). The C-N bond measures 1.39 Å, and C=N is 1.32 Å. None of the distances and angles in the aromatic rings and in the methoxycarbonyl groups differs significantly from the usual values.

The intermolecular distances require no special comment, all corresponding to van der Waals interactions.

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Absolute Integrated Intensity Measurement: Application to CaWO_4 and Comparison of Several Refinements

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A technique for absolute intensity measurement is described which appears capable of establishing an experimental scale to within 1.25% to 1.50% of the true value. A limited amount of data obtained from absolute measurements on CaWO_4 has been compared with a more extensive set of relative data of Zalkin & Templeton. Anisotropic least-squares refinements based on these data as well as neutron data of Kay, Frazer & Almodovar have been compared. The apparent anisotropies of thermal parameters are not entirely consistent between any two experimental techniques. There is evidence for residual systematic error in both X-ray experiments after corrections for absorption, anomalous dispersion, and secondary extinction. As long as some systematic error remains it appears that a limited number of very careful measurements is not as effective for refinement of positional parameters as a very large number of less careful measurements, even for very simple structures.

Absolute intensity measurements have been out of fashion in crystal structure analysis for many years. Originally there was no substitute for such measurements in solving the trial structure stage as exemplified

by the classic work of Warren & Bragg (1928) on diopside. With the introduction of photographic techniques based on small crystals bathed in the X-ray beam a direct experimental determination of the

absolute scale became very difficult. Finally the Wilson (1942) method of determining an approximate scale from statistical considerations made an experimental scale quite unnecessary for the trial structure stage.

Two more recent developments make it desirable to consider again the question of an absolute experimental scale as part of the larger question of valid integrated intensity measurements. The advent of automatic computing has made it possible for the refinement stage to be carried routinely to nearly any desired lengths. The development of electronic systems for photon detection and counting has made it possible for intensity measurements to be made to any desired degree of precision. The random errors in crystallographic data can be reduced to such an extent that the chief uncertainties are of a systematic nature.

The information sought from contemporary refinements includes accurate bond distances and angles, knowledge of thermal motion, and sometimes a knowledge of the electron density distribution. The contributions of Cruickshank (1956) and many others have shown that accurate positional parameters do not of themselves yield the desired bond distances and angles until allowance is made for thermal motion. In the ultimate analysis the accuracy of distances and angles is limited by the errors in the corrections for thermal motion. In the presence of systematic errors the scale factor (or scale factors) and the thermal parameters are not independent of each other. In a sense, then, all of the information desired from detailed refinement, including electron density distributions, is dependent on a knowledge of the absolute scale. It appears worthwhile, therefore, to consider what may be done by direct experimental measurement.

The purposes of this communication are the following:

1. To describe an experimental technique which is appropriate for both valid integrated intensity measurement and the determination of an absolute scale.
2. To discuss the compromises which must be made among various conflicting physical factors.
3. To compare data on CaWO_4 obtained by this technique with a larger body of data on CaWO_4 obtained by Zalkin & Templeton (1964) with a different technique.
4. To compare results obtained from the two X-ray experiments and a neutron experiment by Kay, Frazer & Almodovar (1964).

I. An experimental technique for absolute integrated intensity measurement

1. General considerations

Throughout this paper it is assumed that we are dealing with a crystal which is small enough to be

bathed in the incident X-ray beam, and which has an ideal mosaic texture. Under these conditions, in the absence of extinction, the absolute integrated intensity is given by

$$\frac{E\omega}{I_0} = N^2\lambda^3|F|^2 \left(\frac{e^2}{mc^2}\right)^2 \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} AV \quad (1)$$

where

E is the reflected energy,

ω is the angular velocity of crystal rotation,

I_0 is the incident beam energy per unit area and unit time,

N is the number of unit cells per unit volume,

λ is the wavelength,

$|F|$ is the observed structure factor magnitude,

e, m, c are fundamental constants,

θ is the Bragg angle,

A is the transmission factor,

V is the volume of the crystal.

There are two important differences between this case and the classical one of a crystal plate large enough to intercept the entire incident beam. First, a knowledge of A and V is required (note that A depends on the crystal shape and poses a more stringent requirement than a knowledge of the linear absorption coefficient μ or the thickness of a crystal plate). Second, a knowledge of I_0 is required in that portion of the incident beam which is actually intercepted by the crystal. These requirements will introduce experimental errors that are avoided in the classical measurement.

For $E\omega/I_0$ to be meaningful the same spectral distribution must be measured for both E and I_0 . This requires either a crystal monochromated incident beam or the use of balanced filters to measure both E and I_0 . In either case one wishes to perform the integration of E in such a fashion that all reflections are measured on a common basis. This happens if, in the course of the integrations, each mosaic block in the crystal is exposed to the same intensity of each wavelength in the spectral distribution and all the diffracted rays are received by the detector. This condition is satisfied when the collimation of the incident beam is defined by the crystal and the focal spot rather than by slits, the crystal is rotated sufficiently at a uniform velocity, and the aperture of the detector is large enough. The distribution of intensity along the source (focal spot) will probably not be constant. However, at each point on the source it is presumed that all wavelengths are emitted with a uniform distribution of directions. With sufficient rotation of the crystal this ensures that each mosaic block will sample the entire spectral distribution of every point on the source.

Different conditions prevail when a crystal monochromator is used. The wavelengths in a monochromated beam from a stationary crystal will not have a uniform distribution of directions. In addition, for a given direction in the beam, the intensity

distribution of a given wavelength across a plane normal to the beam will not be constant. The smaller the projected length of the source and the more uniform the distribution of intensity along the source, the smaller these effects will be. Because of these 'structural' effects in a crystal monochromated beam, it appears to the writer that there is an implicit, but unstated, assumption in the classical integrated intensity measurement with a crystal plate. This assumption is that the mosaic texture and diffracting power of the plate is uniform on a microscopic scale across the surface of the plate.

When a small crystal is bathed in a crystal monochromated beam the situation appears more complex than for a large crystal plate. At the very least it would seem necessary to use a very high mechanical precision to position the crystal at exactly the same point in the beam for each measurement. In addition it would appear that the crystal must have such a shape, either spherical or cylindrical, that it always presents a constant cross section in the X-ray beam.

The balanced filter technique was chosen for the present work because it seems to pose less stringent mechanical requirements and to allow more flexibility in the choice of crystal size and shape.

To perform the integrations required for E the $\theta-2\theta$ scan was chosen for a variety of reasons which have been discussed elsewhere (Burbank, 1964). A G.E. goniometer was used with a single-crystal orienter (Furnas, 1957). The work was done manually. To minimize the required scanning ranges Mo radiation was used. The X-ray tube was operated under a fixed set of conditions throughout to avoid introducing any additional scale factors relating to changes of voltage or current. The counting rates were always maintained within a linear range for the detection system so that continuous scans could be used. To accomplish this a set of beam attenuators were required with accurately known attenuation factors. To measure I_0 the beam was put into the linear range in two stages. First, the crystal was replaced by a small aperture with an accurately known area. Second, the beam passing the aperture was brought down to a linear range with a beam attenuator.

2. Operating conditions

A molybdenum tube was operated at 40 kV and 25 mA. This choice was made after trial measurements of the direct beam. With balanced filters we always make a differential measurement, $C = \beta - \alpha$, where C is the net count, β is the count made with the β filter, α is the count made with the α filter. In a direct beam measurement, if the ratio of the energy outside the filter pass band to that inside the band is large, then $\beta \approx \alpha$, $\beta \gg C$, $\alpha \gg C$. Since $\sigma_C = \sqrt{(\beta + \alpha)}$, where σ_C is the standard error in C due to counting statistics, the error in C will be unreasonable. Direct beam measurements at 50 kV with balanced Zr, Y filters gave $\beta \approx 1.04\alpha$, $\beta \approx 24C$,

$\alpha \approx 23C$. At 40 kV this changed to $\beta \approx 3\alpha$, $\beta \approx 1.5C$, $\alpha \approx 0.5C$. Our experience also indicates that if Cu radiation is used with Ni, Co filters the tube should be operated at about 23 kV for direct beam measurements.

3. Balanced filters

The balanced filters were introduced by modifying the entrance beam tunnel. Two small, vertical, cylindrical drums were inserted in tandem in the tunnel. Metal foils were mounted on frames which could be raised or lowered inside the drums. Dimensions were chosen so that the drums could be rotated up to 45° with a beam defined by a crystal 0.5 mm in diameter and a source 15 mm long viewed at a take-off angle of 10° .

Metal foils of pure Zr and Y were chosen with a thickness of about 1.5 mil. With this thickness after final adjustment of the drums about 75% of the $K\alpha$ output of the X-ray tube was transmitted. For the balancing procedure the goniometer was operated as a spectrometer with a large Si crystal plate cut parallel to the (111) planes and a 0.02° receiving slit. The X-ray tube could be operated at any voltage up to 50 kV without exciting $\lambda/3$ for Si (111). The Mo $K\alpha$ line occurs at about $13^\circ 2\theta$ and the balance was checked over the range from 3° to 21° or about from 0.25 Å to 1.15 Å. Contrary to Kirkpatrick (1939) a balance to within 0.1% at any point in this range was obtained without need for a third filter element. Possibly this results from the high purity of the metal foils. The balance was observed both by slow scans of $0.2^\circ 2\theta \cdot \text{min}^{-1}$ with the recorder set to show the regions outside the pass band at nearly full scale deflection and also by fixed point counts. Within the accuracy of observation the balance was equally good at either 40 kV or 50 kV with no further adjustment.

4. Beam attenuators

A series of beam attenuators was constructed containing from one to nine 2-mil Zr foils. These were mounted in a holder between the crystal and detector. The attenuation factors were measured for the pass band with the Si (111) spectrometer and the balanced filters. The unattenuated beam intensity in the pass band was first measured by a slow scan with each of the balanced filters, then the attenuated beam was measured in the same way. The attenuation factors ran up to about 140 so to keep within the linear range with good statistics only about half the series could be measured with a given set of receiving slits and X-ray tube current. Four different sets of conditions were used to permit extensive cross correlation and estimates of error. The errors are estimated to run from about 0.5% for the smallest factor of ~ 1.7 to 1.5% for the largest factor of ~ 140 . The first one or two members of the series are used to integrate very strong reflections in a linear range. The last one or two members are needed for direct

beam measurement. The intermediate members were used only to obtain a consistent series. Two methods were used to show that the spectral distribution of the pass band is not altered when the balanced filters and attenuators are used together. First, the attenuation factor for a single foil was found to be constant when measured with every member of the series. Second, scans were made with the recorder exactly as in the balancing procedure, which showed that the balance was maintained for every member of the series.

5. Direct beam measurement

To reduce the area of the direct beam a platinum aperture with a nominal diameter of $70\ \mu$ from a Siemens electron microscope was mounted in the center of a 1 cm by 1 cm square silver plate about 1 mm thick. The plate was mounted on a eucentric goniometer head which could be mounted on the single-crystal orienter. The plate could be adjusted so that it was normal to the X-ray beam by optical means. Optical measurement with a micrometer eyepiece established the aperture diameter to an accuracy of 0.5%. When this aperture was combined with an ~ 80 -fold attenuator, direct beam β and α counts were of the order of 7000 and 2500 c.p.s. An area factor accurate to 1.0% and an attenuation factor accurate to 1.39% give an over-all reduction factor of about 2.3×10^6 , accurate to 1.71%. Thus the intensity in a small cross section of the incident beam about 3.7×10^{-5} cm² in area can be measured to an accuracy of 1.71% at a given time, since the error due to counting statistics can be made quite negligible. To ascertain the 'structure' in the beam the elevator motion of the goniometer head was combined with the χ motion of the single-crystal orienter. The aperture could be placed at the geometric center of the spectrometer by optical means. Then the beam was observed at increments of $\pm \frac{1}{4}$ turn of the elevator motion at $\chi = 0^\circ$ and 90° . At each setting of the aperture a differential measurement was made with the β and α filters. A typical result is shown in Fig. 1. Because of the structure of the beam, I_0 in equation (1) will be given by

$$I_0 = (\text{reduction factor}) \langle I \rangle$$

where $\langle I \rangle$ is an averaged value of measurements throughout the cross section of the beam occupied by the crystal. From Fig. 1 it is obvious that the smaller the crystal the more uniform the intensity it can be measured with. There is an upper limit of about 0.9 mm for a crystal of circular cross section. For measurements reported below with a 0.445 mm crystal the beam uniformity is estimated at 1.83%. This combined with the uncertainty in the reduction factor gives an error in I_0 of 2.50% at a given time. Over a period of six months, a downward drift of about 3.5% was found in I_0 . Allowing an uncertainty

of 0.6% with time for measurements made over a one-month period an over-all error of 2.57% in I_0 is estimated for the results that follow.

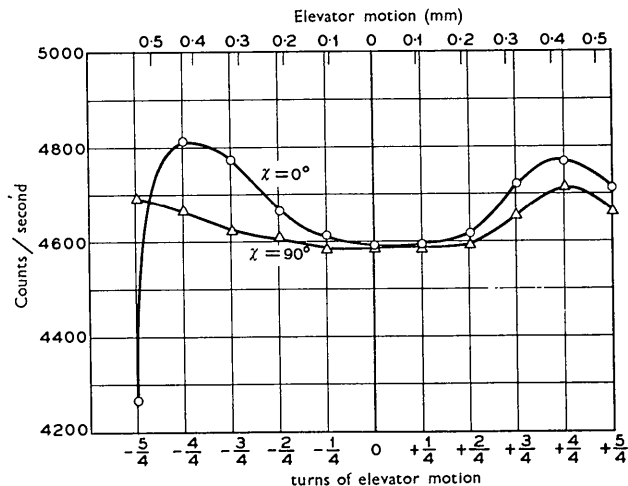


Fig. 1. Structure of an incident beam from a molybdenum target at 40 kV, 25 mA, 3.4° take off, measured with a $\sim 70\ \mu$ circular aperture, ~ 80 -fold attenuation with Zr beam attenuator, and Zr, Y balanced filters. I_0 in the pass band in counts per cm² sec is approximately 10^{10} at any point in space that would be occupied by a crystal less than 0.9 mm in diameter.

6. Crystal size and shape

The quantity we are ultimately interested in is, from equation (1),

$$|F| = k \left(\frac{E}{2 \sin 2\theta} \right)^{\frac{1}{2}} A \quad (2)$$

where

$$k = \left[\frac{\omega}{I_0} / N^2 \lambda^3 \left(\frac{e^2}{mc^2} \right)^2 V \right]^{\frac{1}{2}} \quad (3)$$

The relative value of $|F|$ depends only on E and A while the scale factor, k , depends on I_0 and V . Depending on the choice of crystal size and shape it would be possible to obtain an accurate scale factor and quite inaccurate structure factors, or excellent relative structure factors and a very poor scale factor. Clearly some sort of compromise is required. In general it is very difficult to measure V directly with any accuracy. If V is obtained indirectly from the density and weight the microbalance sets a lower limit on the size of the crystal. If a balance has a precision of $1\ \mu\text{g}$ and an accuracy of $2\ \mu\text{g}$ the crystal must weigh $200\ \mu\text{g}$ to attain an accuracy of 1% in V . As long as absorption corrections are being made the size of the correction, $A^* = A^{-1}$, does not matter, but the accuracy of the correction is important. For spherical crystals the error in A^* resulting from a given error in μR , where μ is the linear absorption coefficient and R is the crystal radius, can be derived from the tables of A^* versus μR and θ given by Bond

(1959). In Fig. 2 the error in A^* resulting from a 10% error in μR is given for the range covered by the tables. A perhaps unexpected result is that the errors reach a maximum and then actually decrease or at worst remain constant with increase in μR . A practical consequence for crystals of very large μ is that a hundredfold reduction in crystal volume may produce a negligible decrease in the errors in A^* .

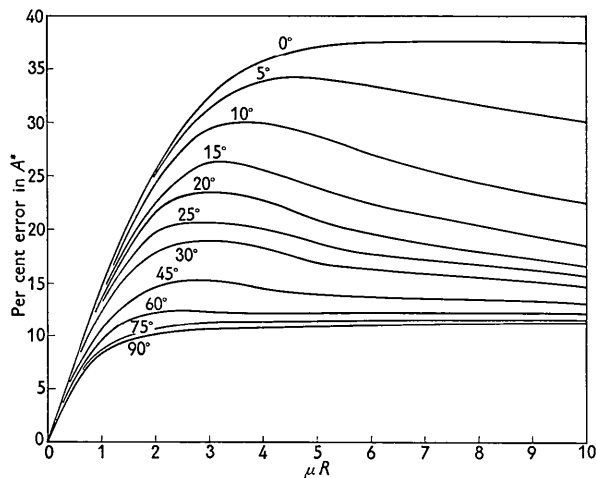


Fig. 2. Series of curves showing percentage error in the absorption correction, A^* , for a spherical crystal, as a function of μR , for a range of values of θ , assuming a 10% error in μR .

The compromise made for the study of CaWO_4 was a spherical crystal which weighed $279 \pm 2 \mu\text{g}$. The resulting uncertainty of 0.72% in V combined with the error of 2.57% in I_0 gives an error of 2.67% in k^2 , or 1.34% in k . The calculated diameter is 0.445 mm and $\mu R = 9.47$. From optical measurements with a micrometer eyepiece the diameter of the crystal is estimated to vary $\pm 5\%$ in different directions. The resulting errors in A^* are assumed to be about half those shown in Fig. 2.

7. Integrated reflections

The intensity curves obtained with well balanced β and α filters will superimpose outside the pass band only for special conditions such as were used in the balancing procedure. Under the conditions used for integrating reflections a variety of unwanted scattering will fall within the pass band arising from such sources as Compton scattering, thermal diffuse scattering, and general parasitic scattering. Fig. 3 illustrates the typical appearance of the reflection curves. The integration extends from $2\theta_1$ to $2\theta_2$ where

$$\begin{aligned} 2\theta_1 &< 2\theta_{Zr(K \text{ edge})} - S - C - M \\ 2\theta_2 &> 2\theta_{Y(K \text{ edge})} + S + C + M \end{aligned}$$

and S , C , and M are the source size, crystal size, and mosaic spread expressed in angular units (Furnas,

1957; Burbank, 1964). The β curve recorded with the Zr filter, and the α curve recorded with the Y filter, do not coincide in intensity at $2\theta_1$ and $2\theta_2$.

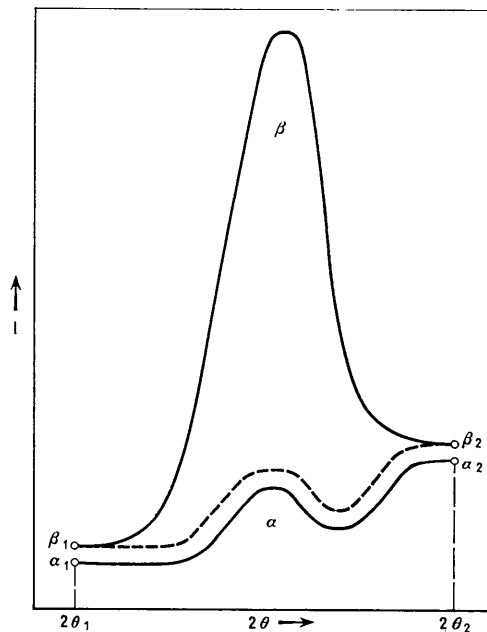


Fig. 3. Typical appearance of reflection curves obtained with balanced filters and $\theta - 2\theta$ scan under conditions suitable for valid integrations.

The required net count is not given simply by $C = \beta - \alpha$. There is an additional background component between the dotted curve and the α curve in Fig. 3 which must be measured. For practical purposes, it is assumed that the miscellaneous scattering, γ , is structureless and has a linear variation with 2θ . This, of course, is a compromise because the thermal diffuse scattering does have structure and peaks directly under the reflection peak. The measure of γ is taken to be

$$\gamma = \frac{1}{2}[(\beta_1 - \alpha_1) + (\beta_2 - \alpha_2)] \Delta 2\theta \quad (\text{conversion factor})$$

where β_1 , α_1 and β_2 , α_2 are counting rates measured at $2\theta_1$ and $2\theta_2$. If β and α have been integrated by scanning at $2^\circ 2\theta$ per minute and the fixed counts are made for 100 seconds, then the conversion factor is 0.3 since

$$(0.3) \text{ counts/100 sec} \equiv \text{counts/30 sec} \equiv \text{counts/1}^\circ 2\theta.$$

The net count is given by $C = \beta - \alpha - \gamma$, and the statistical error is assessed as $\sigma_c = \sqrt{C_T}$, where C_T , the total count, is given by

$$C_T = \beta + \alpha + 0.15 \Delta 2\theta (\beta_1 + \alpha_1 + \beta_2 + \alpha_2).$$

If the peak of the β curve is below 10,000 c.p.s. then no beam attenuator is used and $E = C$. If a beam attenuator is used then

$$E = C(\text{attenuation factor})$$

and

$$\sigma_E = \sqrt{(C_T(\text{att. factor})^2 + \sigma_{(\text{att. factor})}^2 C^2)}.$$

The working procedure adopted for each reflection was first to make a double tracing with the recorder using each filter in turn. From this it could be determined if a beam attenuator was required for linear scaling. From the points at which the curves first diverged and later converged the calculated scan limits $2\theta_1$ and $2\theta_2$ were confirmed. Then using the scaler a scan was made with each filter, and fixed counts at $2\theta_1$ and $2\theta_2$ were made with each filter. Such a procedure is not rapid and generally no more than fifteen integrations were performed in any one day.

II. Application to CaWO₄

A crystal of synthetic CaWO₄, prepared by K. Nassau of these Laboratories, was ground into a 0.445 mm diameter sphere. From Mo $K\alpha_1$ observations of the 00 l reflections out to 0,0,28 and of the $h00$ and $0k0$ reflections out to 14,0,0 and 0,14,0 with a 0.02° receiving slit, the unit-cell constants were found to be $a = 5.242_5$, $c = 11.371_5$ Å. These values are in suitable agreement with powder data values of 5.242 and 11.372 (Swanson, Gilfrich & Cook, 1956) and other single-crystal values of 5.243 and 11.376 (Zalkin & Templeton, 1963).

With $S_h = 0.353^\circ$, $S_v = 0.357^\circ$, $C_h = C_v = 0.175^\circ$, and $S_h + C_h + M_h$ measured with balanced filters (Burbank, 1964), M_h was estimated to be 0.5°, where the subscripts h and v refer to directions parallel and perpendicular to a horizontal spectrometer circle. Assuming that $M_v = M_h$, a detector aperture with the horizontal dimension $S_h + 2C_h + 2M_h = 1.703^\circ$, and vertical dimension $S_v + C_v + M_v = 1.032^\circ$, will satisfy the requirements for valid integrations at all values of θ (Burbank, 1964; Furnas, 1957). This requires a minimum diameter of 2° for a circular aperture. To allow for some margin of error in crystal centering and adjusting an aperture with a diameter of 2.3° was used.

The sphere was mounted without any knowledge of the crystal orientation. Adjustments of the goniometer arcs brought the 112 direction of the reciprocal lattice parallel to the φ axis. The reciprocal lattice was examined in a way that is analogous to using zero level precession photographs. The data recorded for a given setting of $\varphi = \varphi_c$, from $\chi = 90^\circ$ to 0° , corresponds to one quadrant of a zero level precession photograph with 112 along the dial axis. The data for $\varphi = \varphi_c + \pi$, $\chi = 90^\circ$ to 0° , correspond to a second quadrant of the same zero level. Eight settings of φ were used to record four classes of reflections,

$$\begin{aligned} & hhl \\ & h, -h+l, l \\ & h, (h+l)/3, l \\ & (k+l)/3, k, l \end{aligned}$$

out to 60° 2θ . At this point we became aware of the work of Zalkin & Templeton (1964), hereafter referred to as ZT, and terminated the measurement program. The four 'zero levels' recorded are the most densely populated levels passing through 112 and are uniformly distributed at about 45° intervals around the 112 axis.

With X-rays the CaWO₄ reflections are of four types,

$$\begin{aligned} 2k+l &= 4n \text{ strong} \\ 2k+l &= 4n+1 \text{ medium} \\ 2k+l &= 4n+2 \text{ weak, oxygen scattering only} \\ 2k+l &= 4n+3 \text{ medium.} \end{aligned}$$

Measurements were made of 104 strong and medium reflections and 39 weak reflections. Of the latter only 6 were observable above background with large errors in counting statistics. For comparison ZT measured 828 reflections. Out of 190 weak reflections only 27 were observable, although 18 of these were in the list of 39 that are common to both experiments. From equation (1) it may be observed that for a given minimum detectable value of $(E\omega/I_0)$, the minimum detectable value of $|F|$ will be smaller for larger values of λ and A . If Mo $K\alpha$ is replaced by Cu $K\alpha$ then λ^3 increases by about 10 and A will decrease. $(E\omega/I_0)_{\min}$ would be expected to decrease because of the decreased output of continuous radiation from a Cu target. When all experimental conditions were held constant except for a change of targets from Mo to Cu it was found that 36 of the 39 weak reflections were observable. This would suggest that to obtain complete experimental data it may often be desirable to use both Cu and Mo radiations, particularly if A is very small.

The standard errors in $|F|$ were estimated by combining the errors in the measurement of E with the errors in the absorption correction and scale factor. To a first approximation the estimated standard errors consist almost entirely of the errors in the absorption correction for the 104 strong and medium reflections which were used in the comparisons that follow.

III. Comparison of three analyses of CaWO₄

Two independent structure analyses of CaWO₄ were completed while the present work was in progress. The X-ray determination by ZT was based on a small trapezoidal crystal fragment and measurement of all reflections out to $2\theta = 100^\circ$ with Mo $K\alpha$, using the stationary crystal technique and β -filtered radiation. The 828 data were corrected for absorption, anomalous dispersion, and extinction, and were given unit weights for least-squares analysis with anisotropic thermal parameters leading to an R value of 0.061. Kay, Frazer & Almodovar (1964, hereafter referred to as KFA) measured 54 different reflections in the $h0l$ and hhl zones by neutron diffraction. The $h0l$ data were corrected for extinction. Anisotropic least-squares analysis with individual weights based on

experimental errors led to an R value of 0.041. These results provide a rather uncommon opportunity to compare two different methods of measuring X-ray reflections and three independent refinements.

For structural refinement with the 104 absolute scale structure factors, the origin of space group $I4_1/a$ was taken at $\bar{1}$ to conform with ZT, and their choice of axial orientation and atomic scattering factors was used. Values for the dispersion corrections, $\Delta f'$ and $\Delta f''$, were taken from *International Tables for X-ray Crystallography* (1962), Table 3.3.2C, with linear interpolation as a function of $\sin \theta/\lambda$ for both Ca and W. ZT incorporated the effect of dispersion into the calculated structure factors. We have followed Patterson's procedure (Patterson, 1963) and eliminated the effect of dispersion from the observed structure factors. For CaWO_4 the correction is of the form

$$|F_o|_a = (|F_o|^2 - D)^{\frac{1}{2}}$$

where

$|F_o|$ is the observed structure factor magnitude,

$|F_o|_a$ is the observed structure factor corrected for dispersion,

and

$$D = 2\delta_{1W}FF_W + 2\delta_{1Ca}FF_{Ca} + (\delta_{1W}^2 + \delta_{2W}^2)F_W^2 + 2(\delta_{1W}\delta_{1Ca} + \delta_{2W}\delta_{2Ca})F_WF_{Ca} + (\delta_{1Ca}^2 + \delta_{2Ca}^2)F_{Ca}^2$$

where

$$\delta_{1W} = \Delta f'_W/f_W, \quad \delta_{2W} = \Delta f''_W/f_W, \quad \text{etc.}$$

F is the calculated, non-dispersive structure factor including thermal motion,

F_W, F_{Ca} are the calculated, non-dispersive contributions of W and Ca to F .

The dispersion corrections were made with a program written by J. L. Bernstein of these Laboratories, which will handle two types of dispersive atom and individual isotropic thermal parameters. The ZT parameters were used with the anisotropic thermal parameters expressed as equivalent isotropic parameters. The error introduced by using B 's instead of β 's is trivial for CaWO_4 . We estimate that if this procedure caused an error of 5% in F, F_W , and F_{Ca} the error in $|F_o|_a$ would range from 0.05% to 0.27%.

The observed structure factors, now including dispersion connections, were next corrected for secondary extinction by means of Zachariasen's revision of the Darwin theory (Zachariasen, 1963). For data on an absolute scale the correction is of the form

$$|F|_{\text{corr}} = |F|_{\text{obs}}[1 + (\alpha/2)(E\omega/I_0)]$$

where

$$\alpha = g_2 \left(\frac{P_2}{P_1^2} \right) V^{-1} \frac{dA^*}{d\mu},$$

g_2 is the secondary extinction coefficient,

$$P_1 = (1 + \cos^2 2\theta)/2 \quad \text{and} \quad P_2 = (1 + \cos^4 2\theta)/2,$$

values of $dA^*/d\mu R$ can be obtained from tables of A^* versus μR and θ for spherical crystals and

$$dA^*/d\mu = RdA^*/d\mu R.$$

Making a plot of $(F_{\text{calc}}/F_{\text{obs}} - 1)$ versus $(\alpha/2g_2)(E\omega/I_0)$, the slope of the best straight line through the points is g_2 . With $g_2 = 500$, the correction was applied to the entire set of data. The largest correction was 13.3% for the 112 reflection. The correction was larger than 5% for four reflections, larger than 3% for nine reflections, and larger than 1% for twenty reflections.

The structure factors corrected for dispersion and extinction are listed in Table 1. The standard errors were carried through the experimental work as percentages and then applied to the corrected structure factors to give the errors in absolute units which are listed in Table 1. To compare these data with the ZT data it was necessary to eliminate the effect of dispersion from the ZT $|F_o|$. The dispersive effect should be directly obtainable from the relation

$$D = |F_c|_a^2 - |F_c|^2$$

where the $|F_c|_a$ are the reported ZT calculated structure factors including the effect of dispersion, and the $|F_c|$ are calculated with the ZT parameters and non-dispersive scattering factors. Use of the above relation suggests that there was an error in the ZT dispersion program. Values of D obtained from $|F_c|_a$ are unreasonably large, often by more than an order of magnitude. The dispersion effects were therefore removed in the same manner as for the absolute measurements. The 828 ZT data, corrected for dispersion, were refined by least squares with the Busing & Levy Program (1959), leading to an R value of 0.058 and somewhat smaller standard deviations than reported by ZT. Fortunately the effects of dispersion are not large for CaWO_4 and there are only minor shifts in structural parameters. However, the scale factor derived from this procedure, required for comparison with the experimental scale, involves an increase of 3.2%. The 104 ZT measurements which are common to the present work are listed in Table 1.

The agreement between the absolute and relative measurements can be expressed in terms of the index

$$\Sigma |F_o - F_{\text{ZT}}| / \Sigma F_o = 0.056.$$

The absolute and relative scales can be compared in terms of the ratio

$$\Sigma F_{\text{ZT}} / \Sigma F_o = 1.019.$$

The absolute data can also be checked by anisotropic least-squares refinement with and without a variable scale factor. When this is done the scale factor changes from 1.000 to 1.012. The estimate of 1.34% error in the experimental scale appears to be reasonable.

In Table 2 the results of several least-squares refinements with anisotropic thermal parameters are

Table 1. Comparison of absolute measurements of F_o and σ with Zalkin & Templeton's relative measurements, F_{ZT}

Both sets of data are corrected for effects of anomalous dispersion and secondary extinction

hkl	F_o	σ	F_{ZT}	hkl	F_o	σ	F_{ZT}	hkl	F_o	σ	F_{ZT}
004	259.5	15.2	249.0	215	126.3	5.73	140.0	352	167.6	6.29	165.1
008	222.3	9.51	218.0	217	112.2	4.76	127.7	363	86.5	3.21	89.0
0.0.12	217.0	8.33	214.0	220	283.4	12.4	259.0	411	94.3	3.98	101.5
0.0.16	124.1	4.50	124.5	224	238.0	10.5	231.5	413	122.4	5.07	126.7
011	155.9	10.5	182.4	228	205.0	8.28	200.4	415	85.6	3.51	97.3
013	158.4	9.57	170.1	2.2.12	175.9	6.49	164.2	4.1.11	67.7	2.60	72.4
033	99.3	4.55	111.0	231	102.2	4.44	102.3	4.1.13	55.0	2.20	57.8
039	75.7	3.09	66.6	233	142.2	6.01	146.4	431	107.8	4.31	104.9
044	192.8	7.90	199.5	235	85.4	3.59	97.4	435	94.9	3.69	101.6
0.4.12	136.1	4.95	142.5	237	80.3	3.28	86.9	437	88.7	3.37	101.5
055	84.3	3.38	86.1	239	97.7	3.81	113.1	439	61.9	2.40	66.9
112	316.9	19.2	304.2	2.3.11	64.7	2.47	77.6	440	159.0	6.07	158.7
116	267.0	12.3	244.1	251	103.7	4.04	106.0	444	182.4	6.82	178.7
1.1.10	209.9	8.40	201.5	253	82.9	3.26	84.8	448	162.7	5.94	151.8
1.1.14	157.5	5.75	150.7	257	69.8	2.67	76.6	451	73.2	2.80	73.1
121	87.9	4.80	93.9	260	158.9	5.83	155.9	457	72.1	2.70	70.3
123	130.1	6.48	147.4	264	157.1	5.73	157.3	512	166.7	6.54	171.4
125	139.4	6.31	146.6	268	127.7	4.62	133.0	516	182.7	6.89	187.2
127	111.8	4.74	129.7	271	62.2	2.40	59.6	521	74.5	2.97	78.5
132	232.7	10.4	223.3	312	252.3	11.3	237.1	523	99.5	3.86	101.7
136	219.0	9.06	232.8	316	183.4	7.61	190.1	527	79.4	2.99	83.8
1.3.10	150.2	5.75	158.0	3.1.10	169.2	6.48	180.9	532	175.3	6.57	169.4
141	121.7	5.09	126.7	321	147.1	6.34	147.6	541	87.9	3.29	80.9
143	101.4	4.23	101.6	323	105.2	4.47	115.1	547	63.9	2.43	65.2
145	81.3	3.35	94.0	325	73.8	3.13	86.5	552	146.1	5.29	142.3
1.4.11	76.2	2.87	86.0	327	74.1	3.05	82.6	613	75.1	2.85	75.6
1.4.13	66.3	2.52	71.4	329	82.4	3.25	98.5	615	86.7	3.23	87.1
152	201.9	7.89	189.2	3.2.11	85.8	3.15	101.6	617	82.2	3.05	78.8
156	136.4	5.16	148.3	332	218.2	8.97	210.9	619	60.8	2.36	61.9
163	74.1	2.82	72.4	336	192.9	7.62	188.0	620	144.0	5.29	144.4
165	80.6	3.03	77.7	3.3.10	170.5	6.26	162.0	624	159.2	5.81	153.8
167	70.1	2.65	76.5	341	85.3	3.46	88.9	628	131.3	4.74	134.2
169	55.9	2.23	59.7	345	106.7	4.14	111.1	633	73.8	2.78	79.5
211	163.0	8.74	169.4	347	89.4	3.40	99.5	721	75.7	2.82	74.6
213	81.5	4.12	90.8	349	67.6	2.58	73.2				

Table 2. Comparison of several anisotropic least-squares refinements of CaWO_4

To facilitate comparisons positional parameters are given in \AA as $X_i = x_i a_i$, where x_i are fractional coordinates, a_i are direct lattice vectors, thermal parameters are given in \AA^2 as $B_{ij} = 4\beta_{ij}/a_i^* a_j^*$, where β_{ij} are dimensionless and a_i^* are reciprocal lattice vectors. KFA refers to neutron data, ZT to relative X-ray data, ZT_d to the same data with experimental values corrected for anomalous dispersion, and F_o to absolute X-ray data. In each case the first entry is the parameter and the second entry is the standard error

	KFA		828 ZT		828 ZT_d		104 ZT_d		104 F_o	
Oxygen positions (\AA)										
X_1	0.790	0.003	0.789	0.007	0.793	0.006	0.764	0.019	0.785	0.010
X_2	0.046	0.003	0.045	0.007	0.041	0.006	0.055	0.019	0.049	0.010
X_3	2.396	0.001	2.402	0.007	2.401	0.006	2.414	0.015	2.385	0.010
Oxygen thermal (\AA^2)										
B_{11}	0.62	0.13	1.10	0.18	1.03	0.15	1.15	0.76	0.69	0.41
B_{22}	0.80	0.15	1.26	0.18	1.25	0.16	1.44	0.68	0.80	0.29
B_{33}	0.82	0.16	0.83	0.16	0.74	0.13	0.06	0.45	0.84	0.39
B_{12}	0.15	0.08	0.18	0.14	0.13	0.12	0.03	0.55	0.34	0.27
B_{13}	0.10	0.05	0.10	0.14	0.13	0.11	0.47	0.55	0.56	0.27
B_{23}	0.12	0.05	0.19	0.14	0.15	0.12	0.46	0.51	0.39	0.24
Calcium thermal (\AA^2)										
B_{11}	0.56	0.24	0.78	0.04	0.73	0.04	1.38	0.22	0.84	0.11
B_{33}	0.98	0.31	0.57	0.05	0.53	0.06	0.48	0.36	-0.32	0.15
Tungsten thermal (\AA^2)										
B_{11}	0.42	0.24	0.40	0.01	0.36	0.01	0.29	0.04	0.33	0.02
B_{33}	0.20	0.27	0.49	0.02	0.45	0.01	0.30	0.07	0.57	0.03
R	0.041		0.061		0.058		0.037		0.032	
$\chi^2/(\sum w\Delta^2/n-m)$	1.578		Not available		4.778		6.882		1.002	

listed. To facilitate comparisons positional parameters and errors are given in \AA , thermal parameters and errors in \AA^2 . The neutron diffraction results are listed under the heading KFA, the original ZT results under

828 ZT. The 828 F_{ZT} corrected for dispersion as described above were refined and are listed under 828 ZT_d . The ZT data common to the absolute measurements were refined and are listed under

104 ZT_a . The results from the absolute measurements are listed under 104 F_o . It will be noted that the correction for dispersion makes no significant change in the ZT analysis beyond slightly reducing the R index and standard deviations. The results obtained with 104 reflections were disconcerting. For 104 ZT_a the oxygen temperature factor is not positive definite because of a very small β_{33} . For 104 F_o the calcium temperature factor is not positive definite and β_{33} is negative. The standard errors for 104 F_o are roughly half those for 104 ZT_a which might be expected if the balanced filter technique gives a closer approximation to the true integrated intensities than the stationary crystal technique. For 104 ZT_a the scale factor increases by 1.2% relative to 828 ZT_a . For 104 F_o , if the scale factor is allowed to vary the increase is also 1.2%, no positional parameter changes by more than 0.001 Å, and no thermal parameter changes by more than 0.05 Å². For 104 F_o if $Ca\beta_{33}$ is reset to $+\sigma$ and held fixed there is no significant change in any parameter.

For 104 F_o the calculated standard deviation of an observation of unit weight is 1.002. This would indicate that the absolute errors listed in Table 1 are reasonably objective.

The apparent anisotropies of the thermal parameters in Table 2 are not entirely consistent between any two experimental techniques as indicated by the following comparison:

$$\begin{array}{ccc} \text{Oxygen} & & \text{Calcium} \\ ZT \quad B_{22} > B_{11} > B_{33} & & ZT \left\{ \begin{array}{l} B_{11} > B_{33} \\ F_o \end{array} \right. \\ KFA \left. \begin{array}{l} F_o \\ \end{array} \right\} B_{33} > B_{22} > B_{11} & & KFA \quad B_{33} > B_{11} \\ \\ & & \text{Tungsten} \\ & & ZT \left\{ \begin{array}{l} B_{33} > B_{11} \\ F_o \end{array} \right. \\ & & KFA \quad B_{11} > B_{33} \end{array}$$

When the data of Table 1 were examined for reflections for which

$$|F_o - F_{ZT}| \geq 3\sigma$$

thirteen were found, all of medium magnitude. These are listed in Table 3 along with the calculated structure factors from the 828 ZT_a refinement. The absolute measurements are consistently on the low side, the relative measurements consistently on the high side. The absolute measurements actually agree more closely with the calculated values as indicated by the ratios

$$\begin{aligned} \Sigma |F_o - ZT_c| / \Sigma F_o &= 0.064, \\ \Sigma |ZT_o - ZT_c| / \Sigma ZT_o &= 0.078. \end{aligned}$$

There appears to be a systematic error throughout these observations which tend to occur in pairs of hkl and $kh\bar{l}$. The existence of two independent sets

Table 3. Reflections from Table 1 for which

$$|F_o - F_{ZT}| \geq 3\sigma$$

Absolute values, F_o , and relative values, ZT_o , are compared with calculated values, ZT_c

hkl	F_o	ZT_c	ZT_o
127	111.8	121.0	129.7
217	112.2	118.4	127.7
145	81.3	87.1	94.0
415	85.6	89.9	97.3
1.4.11	76.2	80.2	86.0
235	85.4	91.0	97.4
325	73.8	78.2	86.5
239	97.7	104.1	113.1
329	82.4	89.0	98.5
2.3.11	64.7	72.3	77.6
3.2.11	85.0	92.1	101.6
347	89.4	93.6	99.5
437	88.7	91.3	101.5

of data is important because it is doubtful if attention would be drawn to discrepancies of 6 to 8% in the ordinary course of events with a single set of data.

Among the possible sources of systematic error are the following:

1. Stability of crystal mounting and orientation.
2. Primary and secondary extinction.
3. Stability of X-ray source and other electronic components.
4. Absorption.
5. Simultaneous diffraction.
6. Thermal diffuse scattering.

Errors from the first two sources would make observations too small, errors from the next two factors might work in either direction, and errors from the last two causes would generally make observations too large.

For the absolute measurements the crystal centering and orientation was checked every day with the 112 reflection at $\chi = 90^\circ$. Extinction can be discounted because the data are on an absolute scale and after the correction for secondary extinction none of the strong reflections are too low. Pulse height analysis was not used and the systematic error is too large to be accounted for by variations in the remaining electrical components. Absorption is the most probable source of the error. If simultaneous diffraction were operative it should have been observed as sharp features superimposed on the peaks which were traced on the recorder for every reflection before integration with the scaler.

For the ZT relative measurements absorption is also the most probable source of the error. In addition thermal diffuse scattering might cause more error in the stationary crystal technique with β -filtered radiation than in the $\theta - 2\theta$ scan with balanced filters.

KFA corrected the W-O distance for thermal motion by 0.003 Å assuming Cruickshank's (1956) result. ZT corrected the W-O distance by 0.005 Å assuming that oxygen 'rides' on tungsten. Considering that there are inconsistencies in the thermal anisotropies from the different experiments, and that there are systematic errors remaining in the X-ray data, the

Table 4. *Apparent size and shape of tungstate group and calcium coordination from four refinements of CaWO₄ without corrections for thermal motion*

Column headings as for Table 2. All calculations are based on a unit cell with $a=5.2425$ $c=11.3715$ Å

		KFA	828 ZT _d	104 ZT _d	104 F _o
Tungstate group					
W	4 O	1.785 ± 0.003 Å	1.788 ± 0.006 Å	1.773 ± 0.018 Å	1.771 ± 0.010 Å
O	2 O	2.879 ± 0.003 Å	2.882 ± 0.010 Å	2.873 ± 0.028 Å	2.852 ± 0.017 Å
O	O	2.986 ± 0.004 Å	2.993 ± 0.012 Å	2.940 ± 0.038 Å	2.972 ± 0.020 Å
2	O-W-O	113.49 ± 0.23°	113.68 ± 0.37°	112.00 ± 1.06°	114.03 ± 0.66°
4	O-W-O	107.50 ± 0.15°	107.41 ± 0.18°	108.22 ± 0.52°	107.24 ± 0.32°
Difference in angles		5.99	6.27	3.78	6.79
Calcium coordination					
Ca	4 O	2.438 ± 0.002 Å	2.436 ± 0.006 Å	2.424 ± 0.016 Å	2.449 ± 0.010 Å
Ca	4 O	2.478 ± 0.005 Å	2.475 ± 0.006 Å	2.509 ± 0.018 Å	2.480 ± 0.010 Å

meaning of such thermal corrections is uncertain. However, there are no large correlation coefficients involving the positional parameters in any of the refinements. Therefore the positional parameters should be unaffected by any uncertainties in the thermal parameters. The apparent bond distances and angles, uncorrected for thermal motion, derived from the KFA positional parameters are taken as a standard for comparing the X-ray results. These quantities depend only on the oxygen positional parameters and are particularly susceptible to determination by neutron diffraction. The neutron scattering lengths are $b_{\text{Ca}}=0.49$, $b_{\text{W}}=0.446$, $b_{\text{O}}=0.577$. For neutron reflections with l odd there is almost no contribution from the heavy metal atoms.

In Table 4 the apparent size and shape of the tungstate group and the calcium coordination are compared for the different refinements. The results for 828 ZT_d agree extremely well with KFA. For 104 F_o the O-20 distances vary by 0.027 Å from KFA. For 104 ZT_d the O-O distance varies by 0.046 Å and one set of Ca-4O distances varies by 0.031 Å from KFA. The greatest difference between the 104 F_o data and the 104 ZT_d data is shown in the results for the O-W-O angles.

The following conclusions seem reasonable concerning the X-ray experiments:

1. The technique for absolute measurement appears capable of determining the scale factor to within 1.25% to 1.50% of the true value.
2. It is extremely difficult to eliminate all systematic error from observed structure factors.
3. As long as some systematic error remains, a limited number of very careful measurements is not as effective for refinement of positional parameters as a very large number of less careful measurements, even for very simple structures.

4. For a reliable knowledge of thermal motions or electron density distributions every conceivable precaution to minimize systematic error should be taken with a very large number of measurements.

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