these crystals may vary easily with the conditions of crystal growth. The lattice energy and the crystal surface energy become of comparable size in such small crystals and therefore the interaction force acting between the crystal or molecules and the substrate is able to have an effect to some extent on the growth process.

The authors wish to express their thanks to Dr K. Ishizuka for providing a computer program for image simulations. Thanks are also due to Mr M. Tsuji for his kind assistance.

References

ADACHI, K., ADACHI, M., KATOH, M. & FUKAMI, A. (1968). *J. Electron Microsc.* **17**, 280.
ASHIDA, M., UYEDA, N. & SUITO, E. (1966). *Bull. Chem. Soc. Jpn*, **39**, 2616–2624.
BROWN, C. J. (1968). *J. Chem. Soc. A*, 2488–2493, 2494–2498.
CLARK, W. R. K., CHAPMAN, J. N. & FERRIER, R. P. (1979). *Nature (London)*, **277**, 369–370.
FUJIYOSHI, Y., KOBAYASHI, T., ISHIZUKA, K., UYEDA, N., ISHIDA, Y. & HARADA, Y. (1980). *Ultramicroscopy*, **5**, 459–468.
KIRNER, J. F., DOW, W. & SCHEIDT, W. R. (1976). *Inorg. Chem.* **15**, 1685–1690.
KOBAYASHI, T. & REIMER, L. (1975). *Bull. Inst. Chem. Res. Kyoto Univ.* **53**, 105–116.
MASON, R., WILLIAMS, G. A. & FIELDING, P. E. (1979). *J. Chem. Soc. Dalton Trans.* pp. 676–683.
MURATA, Y., FRYER, J. R. & BAIRD, T. (1976). *J. Microsc. (Oxford)*, **108**, 261–275.
REIMER, L. (1965). *Lab. Invest.* **14**, 344–358.
ROBERTSON, J. M. & WOODWARD, I. (1940). *J. Chem. Soc. A*, 36–48.
SAIJO, H., KOBAYASHI, T. & UYEDA, N. (1977). *J. Cryst. Growth*, **40**, 118–124.
SCHEIDT, W. R. & DOW, W. (1977). *J. Am. Chem. Soc.* **99**, 1101–1104.
UNWIN, P. N. T. & HENDERSON, R. (1975). *J. Mol. Biol.* **94**, 425–440.
UYEDA, N., KOBAYASHI, T., OHARA, M., WATANABE, M., TAOKA, T. & HARADA, Y. (1972). *Proc. Fifth Eur. Conf. Electron Microsc., Manchester*, p. 566.
WILLIAMS, R. C. & FISHER, H. W. (1970). *J. Mol. Biol.* **52**, 121–123.

Acta Cryst. (1981). A**37**, 697–701

An X-ray Measurement of Charge Asphericity in Vanadium Metal

BY S. OHBA,* S. SATO AND Y. SAITO*

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, *Japan*

(*Received* 3 *December* 1980; *accepted* 9 *March* 1981)

Abstract

For b.c.c. vanadium metal the integrated intensities of 80 independent reflections were measured by using a spherically shaped single crystal 0·241 (3) mm in diameter with Ag *Ka* radiation. It was confirmed that there are very small differences in integrated intensities between paired reflections, and these differences can be measured significantly beyond the experimental error. The ratios of the paired reflections are smaller than those obtained from platy crystals [Weiss & DeMarco (1965). *Phys. Rev. A*, **140**, 1223–1225] but are in good agreement with those recalculated recently by means of the APW method [Wakoh & Kubo (1980). *J. Phys. F*, **10**, 2707–2715].

Introduction

There is asphericity of the charge distribution around atoms in b.c.c. $3d$ metals and this causes a slight difference in the X-ray scattering factors for paired reflections having the same $\sin\theta/\lambda$, such as 442 and 600. Weiss & DeMarco (1965) attempted to detect the integrated intensity differences of the paired reflections using transmission with Mo *Ka* radiation for a vanadium single-crystal plate 0·1 mm in thickness and perpendicular to [110]; they obtained the ratios listed in Table 1. The experimental ratios were much larger than the theoretical values calculated by employing the Green-function method (Wakoh & Yamashita, 1971). Diana & Mazzone (1975) repeated the experiment and obtained the same order of magnitude for the asphericity as that reported previously. A different type of experiment is desirable in order to obtain a clue to the disagreement between the experimental and

---

* Present address: Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223, Japan.

0567-7394/81/050697-05$01.00

Table 1. *Experimental and theoretical ratios of the integrated intensities of the reflection pairs for vanadium metal*

Standard deviations of the experimental ratios are shown in parentheses.

F^2/F^2†	Present study	Wakoh & Kubo (1980)	Wakoh & Yamashita (1971)	Weiss & DeMarco (1965)	Diana & Mazzone (1975)
330/411	1·010 (14)	1·012	1·003	1·025 (10)	1·017 (10)
431/510	1·018 (10)	1·016			
433/530	1·014 (12)	1·009			
442/600	1·014 (16)	1·019	1·006	1·048 (10)	1·040 (20)
532/611	1·007 (10)	1·013			

† The ratio of the paired reflections $h_1k_1l_1$ and $h_2k_2l_2$ is defined as $F^2(h_1k_1l_1)/F^2(h_2k_2l_2)$, where the value of $h_1^4 + k_1^4 + l_1^4$ is always selected to be less than that of $h_2^4 + k_2^4 + l_2^4$.

theoretical results. By the use of a [110] plate, only two reflection pairs, 330–411 and 442–600, can be measured. Thus a study using the conventional technique of X-ray crystal structure analysis with a spherical specimen was undertaken to measure the ratios for more reflection pairs.

Table 2. *Crystal data and experimental conditions*

V (at 297 K)
Cubic, $a = 3{\cdot}0257$ (4) Å, $V = 27{\cdot}70$ (1) Å^3
Space group $Im3m$, $Z = 2$, $\mu(\text{Ag } K\alpha) = 8{\cdot}52$ mm^{-1}
$C_{11} = 22{\cdot}795$, $C_{12} = 11{\cdot}875$, $C_{44} = 4{\cdot}255 \times 10^4$ N mm^{-2} (Alers, 1960)

Diameter of crystal specimen	0·241 (3) mm
Radiation (from a fine-focus Philips tube)	Ag $K\alpha$ ($\lambda = 0{\cdot}5608$ Å)
Monochromator	Graphite plate
Collimator	0·5 mm ⌀
Detector aperture*	8·6 mm ⌀ (2·1°)
$(\sin\theta/\lambda)_{\max}$ of the observed reflections	1·72 Å^{-1}
Scan mode*	ω continuous scan
Scan speed	2° min^{-1} in θ
Scan width*	$(1{\cdot}5 + 0{\cdot}5 \tan\theta)°$
Maximum number of repetitions	4 ($2\theta \leq 120°$) 6 ($120° < 2\theta \leq 150°$)
Criterion to terminate repetition	$\sigma(\lvert F\rvert)/\lvert F\rvert \leq 0{\cdot}003$
Number of reflections measured	1249
Number of non-zero reflections	1246
Number of independent reflections	80

* The peak half-width of reflection 004 was larger than those of 400 and 040. The integrated intensity of 004 measured by the θ–2θ-scan technique using a 5·5 mm ⌀ (1·3°) receiving slit was about 4% less than that measured by the ω-scan technique. However, those of 400 and 040 were not altered. Thus the ω-scan technique with a large scan width of $(1{\cdot}5 + 0{\cdot}5 \tan\theta)°$ was adopted and the receiving slit was kept wide in order to measure the whole intensity.

Experimental

Single crystals of pure vanadium prepared by the floating-zone method were kindly provided by Mr O. Terasaki of Tohoku University. Part of the crystal was cut with a sharp knife and ground by hand with a piece of sandpaper under a stereomicroscope into a nearly perfect sphere 0·241 (3) mm in diameter. After etching with nitric acid, powder diffraction patterns around the Bragg reflections disappeared on a Weissenberg photograph. Intensity measurements were performed on a Rigaku automated four-circle diffractometer at 297 K with Ag $K\alpha$ radiation ($\lambda = 0{\cdot}5608$ Å) monochromated by a graphite plate. The unit-cell constant was determined to be 3·0257 (4) Å from the θ values of twenty reflections equivalent to 541 on a diffractometer with Ag $K\alpha_1$ radiation ($\lambda = 0{\cdot}55941$ Å). This value agreed well with the 3·0285 Å measured for the powder specimens at 300 K (Korhonen, Rantavuori & Linkoaho, 1971). The crystal data are listed in Table 2, together with the experimental conditions. In total, 1249 reflections in the hemisphere of reciprocal space ($l \geq 0$) up to $2\theta = 150°$ were collected with ω scans. Backgrounds were measured by stationary counts on each side of the peaks. The time ratio between background and peak was always greater than 1/3. In the measurement of the lowest five reflections, 110, 200, 211, 220 and 310, Ni-foil attenuators were inserted to make the peak intensity lower than 6000 counts s^{-1}. Their attentuation factors are in the range from 1·3 to 4·1; these were determined from the least squares and their standard deviations are about 0·1% (Fukamachi, 1969). Ag $K\alpha$ radiation was selected because its linear absorption coefficient is about half that for Mo $K\alpha$. However, white X-rays, which cannot be removed by a crystal monochromator or a pulse-height analyzer, are relatively strong owing to the higher excitation voltage of Ag $K\alpha$. In the present work the effect of white X-rays was neglected. At the end of the experiment the intensity of the monochromated incident beam was 98% of that at the beginning. During the period of data collection (8 days), the standard reflections measured every 50 measurements showed no change greater than 1% in $\lvert F_o\rvert$. Thus the scaling of reflection data was neglected. A total of 1246 non-zero reflections were used in the subsequent calculations; these included 80 independent reflections. The intensity data were corrected for Lorentz and polarization effects and for absorption as a sphere with $\mu r = 1{\cdot}03$ (Dwiggins, 1975). The correction for thermal diffuse scattering (TDS) was also made by the program *TDS*2 (Stevens, 1974), which was modified for the ω scan. The elastic constants used are listed in Table 2 (Alers, 1960). For example, the ratios of one-phonon and of two-phonon-included TDS intensity to the Bragg intensity for a scan for 666 ($\sin\theta/\lambda = 1{\cdot}72$ Å^{-1}) are 0·181 and 0·025, respectively. The TDS correction factors for paired reflections having the same $\sin\theta/\lambda$ are almost the same.

The scale and the thermal parameter were refined by the full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). The function minimized was $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where the weight w was defined by $w = \{[\sigma(\text{count.})]^2 + (0{\cdot}015|F_o|)^2\}^{-1}$. The specimen was affected by the anisotropic secondary-extinction effect. The variations of the observed structure factor with the azimuthal angles ψ around the scattering vector are shown in Fig. 1 for 002 and 006. The χ reading was 81° for these reflections, thus the ψ scan was nearly equivalent to the φ scan. A shadow of the crystal specimen by the incident X-ray beam was recorded on a film to confirm that the specimen was not displaced from the center of the beam. Corrections for anisotropic secondary extinction (Coppens & Hamilton, 1970) were applied, where variations of $|F_o|$ with ψ for two reflections, $\bar{1}01$ and 002, were included in the refinement. However, it failed, giving a negative diagonal component of the mosaic-spread tensor. Thus only isotropic correction (Zachariasen, 1967) was applied. The final R $(=\sum||F_o| - |F_c||/\sum|F_o|)$ was 0·026 and $R_w = 0{\cdot}019$ for 80 independent reflections.* The atomic form factor table given by Fukamachi (1971) and the anomalous-scattering coefficients of Cromer & Liberman (1970) were employed. The temperature factor U is 0·00758 (1) Å^2, from which the Debye characteristic temperature is derived to be 340 K, in good agreement with 338 K obtained from a low-temperature specific-heat study (Corak, Goodman, Satterthwaite & Wexler, 1956). It is slightly higher than the 323 K determined from the neutron phonon frequency spectrum (Stewart & Brockhouse, 1958; Weiss & DeMarco, 1965), and lower than the 372 K from the powder X-ray measurement (Linkoaho, 1971).

Results and discussion

The internal agreement factor, $R(F) = \sum||F_o| - \langle|F_o|\rangle|/\sum|F_o|$, of each independent reflection deduced from 5 to 24 equivalent data is plotted in Fig. 2 against the scattering angle, 2θ. Values of the low-angle reflections 110 and 200 rise above the common level. This trend is accounted for by the anisotropic secondary-extinction effect shown in Fig. 1. However, the disagreement of the higher-angle reflections cannot be explained by the secondary-extinction effect. The following two sources of error are possible: (1) an absorption effect, (2) a statistical fluctuation. The first is the error arising from non-sphericity in the crystal shape and can be estimated by the expression given by Jeffery & Rose (1964):

$$\sigma(|F|)/|F| = \frac{\mu r}{2}\left[\frac{1}{A^*}\frac{\mathrm{d}A^*}{\mathrm{d}(\mu r)}\right]\frac{\sigma(r)}{r},$$

where A^* is the absorption correction factor, μ is the linear absorption coefficient, and $\sigma(|F|)/|F|$ and $\sigma(r)/r$ are the coefficients of variation of the structure factor and the radius of a spherical crystal. With the table of $(1/A^*)(\mathrm{d}A^*/\mathrm{d}\mu r)$ published by Flack & Vincent (1978), $\sigma(|F|)/|F|$ was calculated to be 0·004 ~ 0·007 as a function of 2θ and is shown in Fig. 2 by the solid curve. The second is the error from counting statistics and

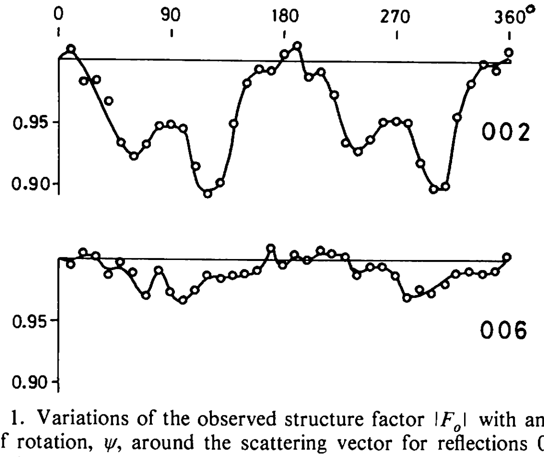

Fig. 1. Variations of the observed structure factor $|F_o|$ with angle of rotation, ψ, around the scattering vector for reflections 002 and 006. Observed values are normalized at $\psi = 0°$, and are shown as open circles.

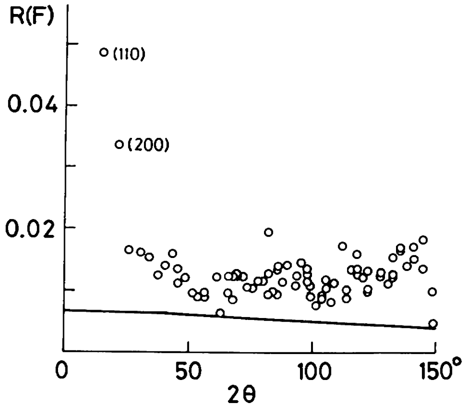

Fig. 2. Plot of $R(F)$, the internal agreement factor, for each independent reflection against 2θ. The solid curve shows the estimated error arising from non-sphericity in the crystal shape.

---

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36074 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. It should be noted that an absolute measurement has not been made in the present study. Thus the structure factors cannot be compared directly with other data on an absolute scale.

intensity fluctuation of the incident beam. It can be estimated roughly from the values of $\langle\sigma(|F_o|)\rangle/\langle|F_o|\rangle$ to be 0·015 ~ 0·019, where $\sigma(|F_o|)$ is defined by $[\sigma(|F_o|)]^2 = [\sigma(\text{count.})]^2 + (0{\cdot}015|F_o|)^2$.

For example, all the observed structure factors of reflection pair 442–600 are listed in Table 3. The intensity variation between equivalent reflections is greater than the difference between the mean values of the independent reflections. However, the fluctuation of the observed structure factor is expected to be random so that it may be cancelled by averaging equivalent reflections. Integrated intensity ratios of the first five reflection pairs are listed in Table 1. Standard deviations of the ratio for the present study were estimated from the statistical errors of the mean structure factors calculated from $\sigma(|F_o|)/n^{1/2}$, where n is the number of equivalent reflections. Let the population of the t_{2g} orbital be α. Then the structure factor can be expressed as: $F(hkl) = 2[f_{\text{core}} + f_{4s} + 4\langle j_0\rangle_{3d} - (10/3)A(hkl)(\alpha - 3/5)\langle j_4\rangle_{3d}]$, where $A(hkl) = 15(h^4 + k^4 + l^4)/2(h^2 + k^2 + l^2)^2 - 9/2$, and the outer five valence electrons are assumed to be in the configuration $(3d)^4(4s)^1$. When α is greater than 3/5, the smaller the $A(hkl)$ is (the smaller the value of $h^4 + k^4 + l^4$ is), the greater the structure factor should be among the reflection pairs. As shown in Table 1 this relation is generally satisfied. Thus, the asphericity of charge distribution in vanadium metal was indeed confirmed by the present experiment. Very recently, Wakoh & Kubo (1980) recalculated the X-ray form factors for vanadium metal by the APW method and it turned out that the charge asphericity obtained from a state-dependent potential is larger than that obtained from the previous state-independent potentials. 'From the viewpoint of the state-independent potentials, the large asphericity obtained by Weiss & DeMarco (1965) has been puzzling for a long time', as Wakoh & Kubo (1980) stated, but now the theory was improved. As discerned from the table, the ratios of the present study agree well with the new theoretical values and are significantly smaller than those obtained from the platy crystals (Weiss & DeMarco, 1965; Diana & Mazzone, 1975). It is premature to discuss the disagreement in the magnitude of asphericity between the experiments using platy or spherical specimens based only on the present result. Other b.c.c. metals should be examined using spherical crystals so that the results may be compared with those obtained from platy ones.

Table 3. *Mean structure factors for* 442, 600 *and all the observed data of their equivalent reflections with estimated standard deviations in parentheses*

4 4 2	6·781 (30)	6 0 0	6·733 (47)
$\bar{4}\,\bar{4}\,2$	6·826 (105)	$0\,\bar{6}\,0$	6·590 (102)
$4\,\bar{4}\,2$	6·745 (104)	$\bar{6}\,0\,0$	6·786 (105)
$\bar{4}\,4\,2$	6·708 (103)	6 0 0	6·788 (105)
4 4 2	6·823 (105)	0 6 0	6·669 (103)
$\bar{2}\,\bar{4}\,4$	6·865 (106)	0 0 6	6·833 (105)
$2\,\bar{4}\,4$	6·725 (104)		
$\bar{4}\,\bar{2}\,4$	6·889 (106)		
$4\,\bar{2}\,4$	6·827 (105)		
$\bar{4}\,2\,4$	6·714 (104)		
4 2 4	6·804 (105)		
$\bar{2}\,4\,4$	6·712 (103)		
2 4 4	6·740 (104)		

The population α of the t_{2g} orbital was estimated from the integrated intensity ratios of the first five reflection pairs, giving 66·6 (2·8)%. The form factor $\langle j_4\rangle_{3d}$ for the V atom was taken from *International Tables for X-ray Crystallography* (1974). The estimated t_{2g} population of 68% from the band calculation employing the state-dependent potential (Wakoh & Kubo, 1980) is in good agreement; however, it cannot be compared directly because the experimental analysis employs the localized atomic model and the value of α depends on the form factors adopted, as pointed out by Diana & Mazzone (1975).

We wish to thank Mr O. Terasaki of Tohoku University for providing us with the single crystals of vanadium metal, and Professor S. Wakoh of the University of Library and Information Science for helpful discussions. We also thank the Ministry of Education for a Scientific Research Grant, from which part of the cost of this research was met. The calculations were carried out on the FACOM 230-48 and FACOM M-160F computers of this Institute.

References

Alers, G. A. (1960). *Phys. Rev.* **119**, 1532–1535.

Coppens, P., Guru Row, T. N., Leung, P., Stevens, E. D., Becker, P. J. & Yang, Y. W. (1979). *Acta Cryst.* A**35**, 63–72.

Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

Corak, W. S., Goodman, B. B., Satterthwaite, C. B. & Wexler, A. (1956). *Phys. Rev.* **102**, 656–661.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Diana, M. & Mazzone, G. (1975). *Philos. Mag.* **32**, 1227–1230.

Dwiggins, C. W. Jr (1975). *Acta Cryst.* A**31**, 395–396.

Flack, H. D. & Vincent, M. G. (1978). *Acta Cryst.* A**34**, 489–491.

Fukamachi, T. (1969). *Jpn. J. Appl. Phys.* **8**, 851–854

Fukamachi, T. (1971). Tech. Rep. ISSP. B, No. 12. Institute for Solid State Physics, Tokyo.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Jeffery, J. W. & Rose, K. M. (1964). *Acta Cryst.* **17**, 343–350.

Korhonen, U., Rantavuori, E. & Linkoaho, M. (1971). *Ann. Acad. Sci. Fenn. Ser. A*6, No. 361, pp. 3–17.

LINKOAHO, M. V. (1971). *Philos. Mag.* **23**, 191–198.
STEVENS, E. D. (1974). *Acta Cryst.* A**30**, 184–189.
STEWART, A. T. & BROCKHOUSE, B. N. (1958). *Rev. Mod. Phys.* **30**, 250–255.
WAKOH, S. & KUBO, Y. (1980). *J. Phys. F*, **10**, 2707–2715.
WAKOH, S. & YAMASHITA, J. (1971). *J. Phys. Soc. Jpn*, **30**, 422–427.
WEISS, R. J. & DEMARCO, J. J. (1965). *Phys. Rev. A*, **140**, 1223–1225.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1981). A**37**, 701–710

An Oscillation Data Collection System for High-Resolution Protein Crystallography

BY M. F. SCHMID, L. H. WEAVER, M. A. HOLMES, M. G. GRÜTTER, D. H. OHLENDORF,
R. A. REYNOLDS, S. J. REMINGTON* AND B. W. MATTHEWS†

Institute of Molecular Biology and Department of Physics, University of Oregon, Eugene, Oregon, USA

(*Received* 13 *November* 1980; *accepted* 25 *March* 1981)

Abstract

An oscillation data collection system for protein crystallography is described. The system consists of a modified Enraf–Nonius precession camera with cylindrical cassette, and stepping motor driven by a flexible microprocessor control system. The X-ray source is graphite-monochromatized radiation from an Elliott GX-21 rotating-anode generator run at 5·5 kW on a focal spot measuring 0·5 × 5·0 mm. The potential advantages of using a relatively large focal spot in conjunction with a graphite monochromator are discussed. Conditions for optimum collimation and X-ray intensity are considered, and it is shown that appropriately designed collimators with adjustable apertures can have substantial advantages over commercially available pinhole collimators. The oscillation films are processed by a procedure based on that of Rossmann [*J. Appl. Cryst.* (1979), **12**, 225–238]. Determination of the initial alignment of the film is facilitated by a pair of reference pins incorporated in the cylindrical cassette. These pins ensure that the position of the film in the cassette is known, and avoid the need for fiducial marks. The crystal alignment and film measurement technique is fully automatic, requiring no prior input other than the approximate starting orientation of the crystal, the approximate unit-cell dimensions, and the angular oscillation range. An alternative method for the determination of crystal orientation is proposed which has been found to be somewhat superior to that of Rossmann, especially for smaller unit cells.

1. Introduction

The use of screenless X-ray photography for the rapid, efficient measurement of diffraction data from protein crystals is well established, and an increasing number of laboratories have developed, and are using, such techniques (*e.g.* Xuong & Freer, 1971; Arndt, Champness, Phizackerley & Wonacott, 1973; Schwager, Bartels & Jones, 1975; Rossmann, 1979; Wilson & Yeates, 1979; and the collection of papers in Arndt & Wonacott, 1977).

In this paper we wish to describe an oscillation data collection system we have developed which includes a number of features we have found to be of value, and may be of interest to other laboratories.

These features include graphite monochromatization to reduce background and enhance crystal life, the use of a broad-focal-spot X-ray generator to reduce exposure times by a factor of four, improved collimation geometry, and cylindrical cassettes for high-resolution data collection. The film scanning program, adapted from that of Rossmann (1979), permits the accurate determination of crystal alignment from the oscillation photograph itself, with no prior input other than the approximate orientation of the crystal. We have adopted an alternative strategy for refinement of the crystal orientation which we have found to work better than the 'convolution' procedure developed by Rossmann for virus crystal photography.

The basic hardware consists of two Enraf–Nonius precession cameras, modified for oscillation photography, each controlled by a microprocessor. The cameras are mounted on an Elliott GX-21 rotating-anode generator with Charles Supper graphite monochromators. Films are scanned by an Optronics P3000 rotating-drum scanner interfaced to a Varian V76

---

* Present address: Max-Planck-Institut für Biochemie, D-8033 Martinsried bei München, Federal Republic of Germany.

† To whom correspondence should be addressed.

0567-7394/81/050701-10$01.00