*Acta Cryst.* (1968). B**24**, 292

# A refinement of the crystal structure of yttrium vanadate.

By J. A. Baglio and G. Gashurov, *General Telephone & Electronics Laboratories Inc., Bayside, New York, U.S.A.*

(*Received* 29 *May* 1967)

The structure of $YVO_4$ has been refined from single crystal and powder X-ray diffraction data. The results confirm the general features of a previous analysis using powder diffraction data, but a considerable improvement in accuracy has been achieved.

Yttrium vanadate, $YVO_4$, crystallizes with a zircon-type structure conforming to the space group $I4_1/amd$ (Broch, 1932). With the origin chosen at the center of symmetry, the yttrium atoms are in 4(*a*): $0,\frac{3}{4},\frac{1}{8}$, *etc*; the vanadium atoms in 4(*b*): $0,\frac{1}{4},\frac{3}{8}$, *etc*; and the oxygen atoms in 16(*h*): $0,y,z$, *etc.* Using powder diffraction data, Broch estimated the oxygen parameters in $YVO_4$ to be $y=0{\cdot}44$ and $z=0{\cdot}23$.

$YVO_4$ activated with trivalent europium ion is a highly efficient luminophor (Levine & Palilla, 1965) and is of considerable theoretical interest. To this end a structure refinement of $YVO_4$ has been carried out with single-crystal diffraction data.

The single crystal of yttrium vanadate chosen for X-ray data collection was a platelet with dimensions $0{\cdot}270\times0{\cdot}146$ $0{\cdot}017$ mm for the **a**, **b**, and **c** directions respectively. The lattice constants, $a=7{\cdot}123$ and $c=6{\cdot}292$ Å, were obtained from powder data and are in good agreement with those measured by Schwarz (1963). The intensity data were recorded with Ni-filtered Cu $K\alpha$ radiation on *hKl* Weissenberg photographs ($K=0\rightarrow5$) by the multiple-film technique. The intensities were estimated visually with calibrating strips and corrected for Lorentz and polarization factors. Ninety-seven independent reflections were recorded. Since the linear absorption coefficient for $YVO_4$ is 475 $cm^{-1}$, intensities were corrected for absorption. The method used was that of Busing & Levy (1957). The direction cosines needed to make absorption corrections for upper layers were calculated from equations derived by Wells (1959).

The single-crystal data were supplemented with powder data in the final refinement. The powder data were collected with crystal-monochromatized Cu $K\alpha$ radiation. The intensities were measured with a scintillation counter equipped with a pulse height analyzer and a printer for recording the data. Counts were accumulated at a fixed time of 100 seconds for each angular interval of 0·02°. Forty-three peaks were recorded, twenty-nine of which were nonoverlapping. Several different packing procedures were used to check reproducibility of measured intensities. It was found that only the 0*k*0-type reflections were strongly dependent on the packing arrangement used.

The single-crystal data were placed on a common scale by a comparison of the structure factors of the single-crystal reflections with those of equivalent powder reflections. Single-crystal reflections of high intensity as well as powder reflections affected by preferred orientation were not included in this scaling procedure.

In structure-factor calculations we used Cromer & Waber's (1965) values for the scattering factors of $Y^{3+}$ and $V^{5+}$, and Cromer's (1965) values of $\Delta f'$ for Y and V. No imaginary dispersion corrections were used. The atomic scattering factors for $O^{2-}$ were those evaluated by Tokonami (1965). Refinement was carried out by a full-matrix least-squares method. The function minimized was $\Sigma\,\omega(F_o-F_c)^2$ with $\sqrt{\omega}=36/|F_o|$ for $|F_o|>36$, and $\sqrt{\omega}=1$ for $|F_o|\le36$. The initial positional parameters for oxygen were those of Broch (1932). The initial isotropic thermal parameters were assumed to be 1 $Å^2$ for all three atoms. Using single-crystal data only, the value of the discrepancy index,

Table 1. *Final coordinates and standard deviations*

Origin at center of symmetry; estimates of standard deviations are given in parentheses.

Positional parameters

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Y | 0 | $\frac{3}{4}$ | $\frac{1}{8}$ |
| V | 0 | $\frac{1}{4}$ | $\frac{3}{8}$ |
| O | 0 | 0·4346 | 0·2023 |
| | | (0·0012) | (0·0013) |

Thermal parameters × 1000
$\{\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{23}kl+\beta_{13}hl+\beta_{12}hk)]\}$

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{23}$ | $\beta_{13}$ | $\beta_{12}$ |
|---|---|---|---|---|---|---|
| Y | 5·3 | 5·3 | 6·1 | 0·0 | 0·0 | 0·0 |
| | (0·4) | (0·4) | (0·7) | | | |
| V | 8·7 | 8·7 | 7·6 | 0·0 | 0·0 | 0·0 |
| | (0·7) | (0·7) | (1·3) | | | |
| O | 11·4 | 8·8 | 11·2 | −11·9 | 0·0 | 0·0 |
| | (5·4) | (2·0) | (3·9) | (6·1) | | |

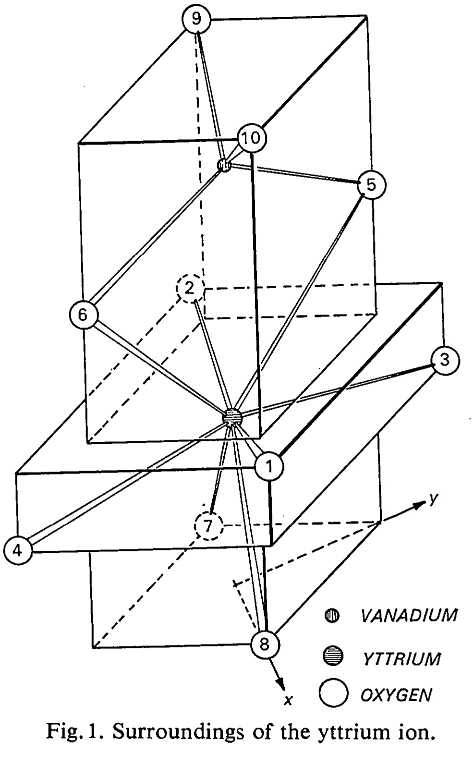

Fig. 1. Surroundings of the yttrium ion.

$\Sigma\, |F_o - |F_c||/\Sigma\, F_o$, was 11 % after six cycles of least squares, anisotropic temperature factors being used in the final three cycles.

Inspection of observed and calculated $F$ values showed that strong reflections were significantly affected by extinction. To minimize the extinction effects, the single crystal $F_o$'s for strong reflections ($F_o \geq 100$) except for 020 and 040 peaks were replaced by the corresponding powder structure factors. Both single-crystal and powder data were placed on a common scale by comparing observed structure factors with those calculated in the preceding refinement. The 020 and 040 reflections, together with unobserved reflections, were given zero weight in the least-squares cycles, although included in the final calculation of the $R$ index. The refinement of these combined single-crystal and powder data was complete after three cycles, giving $R = 6{\cdot}7$ %. Table 1 gives the values of the positional and thermal parameters. Observed and calculated structure factors (final refinement) are listed in Table 2. Table 3 lists interionic distances and angles computed from the structural parameters determined in the present work, and Fig. 1 shows that part of the unit cell which is relevant to the values listed in Table 3.

Table 2. *Observed and calculated structure factors*

For unobserved reflections the values are $(10/\sqrt{3})F_{\min}$, where $F_{\min}$ is the minimum $F$ observed in the corresponding region of reciprocal space; those values are marked with an asterisk.

| $hkl$ | $10F_o$ | $10F_c$ | $hkl$ | $10F_o$ | $10F_c$ | $hkl$ | $10F_o$ | $10F_c$ |
|---|---|---|---|---|---|---|---|---|
| 004 | 1091 | 1209 | 127 | 317 | 285 | 273 | 169 | 141 |
| 008 | 535 | 559 | 132 | 1636 | 1627 | 280 | 615 | 561 |
| 011 | 387 | 398 | 134 | 248 | 272 | 332 | 1517 | 1576 |
| 013 | 734 | 753 | 136 | 803 | 786 | 336 | 585 | 573 |
| 015 | *40 | 95 | 141 | 258 | 218 | 341 | 565 | 502 |
| 017 | 119 | 144 | 143 | 337 | 341 | 343 | 159 | 160 |
| 020 | 1715 | 2118 | 145 | 248 | 259 | 345 | 238 | 230 |
| 022 | 654 | 632 | 147 | 228 | 215 | 352 | 991 | 1023 |
| 024 | 1239 | 1275 | 152 | 1061 | 996 | 354 | 248 | 228 |
| 026 | *50 | 52 | 154 | 79 | 73 | 356 | 644 | 642 |
| 031 | 882 | 891 | 156 | 813 | 852 | 361 | 426 | 410 |
| 033 | 367 | 380 | 161 | 268 | 251 | 363 | 268 | 239 |
| 035 | 89 | 76 | 163 | 426 | 380 | 365 | 119 | 109 |
| 040 | 1685 | 1774 | 165 | 159 | 120 | 372 | 813 | 820 |
| 042 | 297 | 249 | 172 | 863 | 814 | 374 | 59 | 64 |
| 044 | 1061 | 1013 | 181 | 149 | 156 | 381 | 218 | 259 |
| 046 | *30 | 31 | 183 | 129 | 150 | 440 | 1041 | 1099 |
| 051 | 218 | 183 | 220 | 1110 | 1132 | 444 | 912 | 874 |
| 053 | 555 | 531 | 224 | 1358 | 1327 | 451 | 129 | 144 |
| 055 | *89 | 99 | 231 | 565 | 601 | 453 | 288 | 306 |
| 060 | 1110 | 1348 | 233 | *40 | 28 | 455 | 208 | 218 |
| 062 | *59 | 30 | 235 | 327 | 346 | 460 | 932 | 928 |
| 064 | 872 | 735 | 237 | 208 | 205 | 462 | 79 | 80 |
| 071 | 327 | 319 | 240 | 1130 | 1176 | 464 | 714 | 657 |
| 073 | 337 | 306 | 242 | 149 | 122 | 471 | 238 | 242 |
| 080 | 843 | 737 | 244 | 1100 | 1065 | 473 | 149 | 182 |
| 082 | 198 | 167 | 251 | *69 | 87 | 480 | 535 | 541 |
| 091 | 248 | 257 | 253 | 278 | 270 | 552 | 714 | 711 |
| 112 | 1705 | 1579 | 255 | 307 | 318 | 561 | 149 | 169 |
| 116 | 1011 | 1049 | 260 | 991 | 1013 | 563 | 278 | 317 |
| 121 | 129 | 117 | 262 | 188 | 180 | 572 | 506 | 596 |
| 123 | 228 | 247 | 264 | 843 | 781 | | | |
| 125 | 367 | 393 | 271 | 238 | 248 | | | |

Table 3. *Interionic distances and angles*

| | Distances | | Angles |
|---|---|---|---|
| Y-O(1) | 2·299 ± 0·008 Å | O(1)-Y-O(2) | 155·6 ± 0·4° |
| | | O(1)-Y-O(3) | 92·6 ± 0·4 |
| Y-O(5) | 2·443 ± 0·008 | O(5)-Y-O(6) | 65·1 ± 0·4 |
| | | O(5)-Y-O(7) | 135·3 ± 0·4 |
| V-O | 1·706 ± 0·008 | O(5)-V-O(6) | 100·9 ± 0·4 |
| | | O(5)-V-O(9) | 113·9 ± 0·4 |

Grateful acknowledgment is made to Mr T. Peters for supplying single crystals of $YVO_4$ and to Mr A. A. Calvano for his help in taking X-ray measurements.

### References

Broch, E. (1932). *Z. phys. Chem.* **20B**, 345.
Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180.
Cromer, D. T. (1965). *Acta Cryst.* **18**, 17.
Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.
Levine, A. K. & Palilla, F. C. (1965). *International Symposium on Luminescence* (Editors: Riehl, N. & Kallmann, H.). München: Verlag Karl Thiemg.
Schwarz, H. (1963). *Z. anorg. allg. Chem.* **322**, 143.
Tokonami, M. (1965). *Acta Cryst.* **19**, 486.
Wells, M. (1960). *Acta Cryst.* **13**, 722.

---

*Acta Cryst.* (1968). B**24**, 293

## On versions of a procedure for scaling X-ray photographs.

By G. C. Ford and J. S. Rollett, *University Computing Laboratory,* 19 *Parks Road, Oxford, England*

(*Received* 18 *August* 1967)

Two modifications of a method for placing batches of X-ray data on a common scale have been proposed. One of these is an iteration which converges very slowly, and hence yields results with computing errors which are difficult to estimate reliably. This note describes an alternative which gives better convergence and suggests circumstances in which particular methods will be quickest.

The scaling method devised by Hamilton, Rollett & Sparks (1965) (HRS) has been modified by Fox & Holmes (1966) (FH), who found a more appropriate, but slightly more difficult, method of solving the singular set of simultaneous equations for the scale-factor changes. Monahan, Schiffer & Schiffer (1967) (MSS) have proposed a modification which gives a set of independent equations for the scale factors. In this note we show that the MSS method converges very slowly on the test case used by HRS and FH so that any convergence criterion based on the size of the shifts may allow large errors in the results. We therefore describe an approximation to HRS which yields faster convergence than the MSS method. Convergence rates are given in Table 1 and we indicate circumstances in which particular methods are likely to be useful.

Table 1. *Numbers of iterations required to reduce the maximum indicated shift in a scale-factor to various levels*

| | Maximum shift in any scale factor | | | | |
|---|---|---|---|---|---|
| Method | 0·5 | 0·05 | 0·005 | 0·0005 | 0·00005 |
| FH | 3 | 4 | 5 | 6 | 7 |
| HRS | 4 | 5 | 6 | 7 | 8 |
| FR | 6 | 7 | 9 | 12 | 16 |
| MSS | 3 | 14 | 55 | > 126 | |

The 14 parameter problem used as a test was that employed by HRS, FH. The final $G_p$ varied from 0·7884 to 6·0622 and the initial $G_p$ were unity. The value of $G_1$ was kept at unity throughout.

These methods minimize $\sum_h \sum_p w_{hp}(F_{hp}^2 - G_p F_h^2)^2$ with respect to $G_p$.