THE CRYSTAL STRUCTURE OF VANADIUM DIFLUORIDE: RELIABILITY TEST OF HYPOTHETICAL INTENSITY VARIANCES BASED ON χ^2 DISTRIBUTIONS (*)

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ABSTRACT — X-ray integrated intensities from two different crystals of VF_2 have been collected using a CAD4 diffractometer.

Statistical tests of the experimental results were performed: a better agreement with the theoretical χ^2-distribution was found when the Poisson variances, σ^2_ρ, were multiplied by a parameter, v , which was subsequently refined.

A least-squares refinement yielded the values of the positional parameter, x , of the fluoride atom, as well as the anisotropic temperature parameters for both vanadium and fuorine atoms. The results are discussed in terms of the reliability (R-) factors and goodness-of-fit (g.o.f.) parameters obtained.

1 — INTRODUCTION

Vanadium difluoride (VF_2) has a rutile type structure with space group $P4_2/mnm$. The heat capacity, magnetic ordering and

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crystal structure of this compound were investigated by Stout and Boo [1]. Using a needle shaped crystal these authors determined the lattice parameters as

$$a = b = 4.804 \pm 0.005 \text{ Å} \quad \text{and} \quad c = 3.237 \pm 0.005 \text{ Å}$$

From a set of visually estimated intensities difracted by a polycrystalline sample, they obtained the position parameter of the fluorine atom in the unit cell, $x = 0.306 \pm 0.005$, and the isotropic temperature factors for the constituent atoms, namely, $B_V = 0.37$ Å^2 and $B_F = 0.70$ Å^2.

The present work on VF_2 was undertaken as part of a program of electron density determination in several rutile type compounds.

2 — DATA COLLECTION

Two single crystals (A and B), used in the intensity measurements which will be described, were obtained from a large single crystal of VF_2 grown by B. J. Garrard [2], Clarendon Laboratory, Oxford, England.

Since the material is highly opaque, optical tests with polarized light were not possible and the choice of crystals was based on the observation of their shape and size only.

Crystals A and B, although rather irregular in shape, could be described as small blocks of dimensions $(0.05 \times 0.06 \times 0.13)$ mm and $(0.04 \times 0.05 \times 0.10)$ mm, respectively.

The reflection intensities were collected on an automatic X-ray single crystal diffractometer, CAD4, using AgKα radiation and a graphite monochromator. The experiment was carried out at a constant temperature of 20°C stabilized to ± 1°C.

The intensity distribution over a cross-section of the primary beam was checked. The region of maximum intensity was found to be an ellipse having the smaller axis perpendicular to the equatorial plane. Maximum intensity fluctuations of ± 7 % and

$\pm 14\,\%$ were observed along the normal to that plane within 0.1 mm and 0.14 mm respectively.

Using the standard technique developed for the CAD4 diffractometer the lattice parameters were determined as:

$$a = b = 4.808 \pm 0.002 \text{ Å and } c = 3.239 \pm 0.003 \text{ Å}$$

The integrated intensities of all reflections out to $(\sin \theta)/\lambda = 0.9$ Å^{-1} were collected during $\omega - 2\theta$ scans.

Several independent measurements of a number of integrated intensities were carried out for both crystals. These will be referred to, hereafter, as «repeatedly measured intensities».

3 — STATISTICAL TREATMENT

Intensities of Bragg reflections with an asymmetric background were rejected; the remaining 997 integrated intensities from crystal A and 696 from crystal B were used in subsequent statistical tests.

The distribution function of twice measured intensities from both crystals, $F_0(\chi_0^2, \nu)$, was compared with the theoretical distribution function, $F(\chi^2, \nu)$, where $\nu = n - 1$, n being the number of degrees of freedom (n = 2, in the present case). For this comparison, several values of $\chi_0^2 = (n_j - 1)\, s_j^2/\sigma_0^2\,(I_j)$ were chosen, which will be denoted by χ_{0i}^2; the corresponding $F_0(\chi_{0i}^2, \nu)$ were calculated and compared to $F(\chi_i^2, \nu)$. The differences

$$y_i = F(\chi_i^2, \nu) - F_0(\chi_{0i}^2, \nu) \qquad \text{with } i = 1, 2, \ldots m$$

were used to compute the statistical R-factors

$$R = \left(m^{-1} \sum_{i=1}^{m} y_i^2 \right)^{1/2}$$

These are a measure of the agreement between the observed and the theoretical χ^2-distribution.

In the present work, the Poisson variances σ_ρ^2 were replaced by $v\,\sigma_\rho^2$ and the parameter v was refined as suggested by Gonschorek [3].

The experimental data have been compared with both the theoretical and the asymptotic χ^2-distribution. The corresponding R-factors, R and R_{asympt}, respectively, are shown in Table 1. This table summarizes the results of the statistical treatment which has just been outlined; γ is a parameter which defines the time spent in the measurement of each reflection; this is chosen so that $\sigma_\rho(I)/I < \gamma$, $\sigma_\rho(I)$ being the square root of the Poisson variance of the measured integrated intensity, I.

TABLE 1

		Crystal A	Crystal B
Total number of reflections		997	696
$\gamma > \sigma_\rho(I_{ji})/I_{ji}$		0.1	0.005
Twice measured reflections	Number of reflections	154	54
	v	1.20	1.54
	R	0.023	0.031
Symmetry equivalent reflections	Number of reflections	99	82
	$R_{asympt.}$ (without abs. corr.)	0.034	0.031
	$R_{asympt.} \left\{ \begin{array}{l} \text{with abs. corr.} \\ 0.82 \leqslant A \leqslant 0.88 \end{array} \right.$	0.025	—

In Table 2, data obtained for both crystals are compared on the basis of the asymptotical χ^2-distribution proposed by Gonschorek [3] and of the theoretical χ^2-distribution. The number of groups having the same number, n_s, of symmetry equivalent reflections is denoted by $K(n_s)$.

TABLE 2

	Crystal A + Crystal B
Number of common reflections	72
R [$n = 2$; $K(2) = 72$]	0.12
Number of rejected reflections (χ^2-test; $\alpha = 0.1$)	11
$R_{\text{asympt.}}$	0.07
R [$n = 2$; $K(2) = 61$]	0.07

4 — DATA REDUCTION

The two sets of intensities from crystals A and B, respectively, were corrected in the usual way for Lorentz and polarization factors; for the latter correction the monochromator was assumed to be 50 % ideally perfect and 50 % ideally imperfect and set at a Bragg angle, $\sigma_M = 4.55°$.

Absorption factors for each reflection were computed using the Gaussian quadrature program of the CAD4 diffractometer and the absorption coefficients listed for the vanadium and fluorine atoms in «International Tables for X-Ray Crystallography», vol. IV. For crystal A the absorption correction was found to improve the statistical agreement between symmetry equivalent reflections.

For crystal B, the asymptotic R-factor for symmetry equivalent reflections is the same as the theoretical R value for twice measured reflections. This has been taken as an indication that the absorption correction would not improve the data.

The intensities were corrected for anisotropic atomic vibrations; the refined values of the temperature parameters are shown in Table 3.

Atomic scattering factors for the spherical neutral atoms were used in the calculation of structure factors; these and the real and imaginary parts of the anomalous dispersion corrections were calculated using data given in «International Tables for X-ray Crystallography».

Extinction is likely to affect X-ray integrated intensities, particularly those corresponding to the largest observed structure amplitudes, usually occurring at small $(\sin\theta)/\lambda$ values. Several corrections have been proposed to account for this effect; instead of using one of them, at this stage of the present work an attempt was made to avoid or at least to minimize the extinction effects, by selecting a variety of crystals of different sizes and using the shortest possible wavelength ($\lambda_{\mathrm{AgK}_\alpha} = 0.5609$ Å).

TABLE 3

	V	F
μ_{11} (Å)	0.0073(1)	0.0129(3)
μ_{33}	0.0063(2)	0.0085(3)
μ_{12}	−0.0006(2)	0.0056(3)
X	—	0.3053(2)
μ^2_{110} (Å^2)	0.0067(3)	0.0073(6)
$\mu^2_{\bar{1}10}$	0.0079(3)	0.0185(6)
μ^2_{001}	0.0063(2)	0.0085(3)
μ^2	0.0070	0.0114

In order to decide whether or not the integrated intensities are affected by extinction, a few arguments can be used. One of them is based on the statistical treatment that has been described. Extinction is most probably anisotropic in an irregularly shaped crystal; therefore, symmetry equivalent reflection intensities are affected differently.

This should lead to an enhancement of the corresponding χ^2 value taken over symmetry equivalent intensities. Hence, the χ^2 test itself should make a preliminary selection of those reflections which are less seriously affected by extinction.

A further argument can be given which is based on the independent refinement of both crystal data sets. A scale factor, S, was refined using all reflections with $|F_{\mathrm{calc}}| < E$, for different values of E. Table 4 shows the results obtained for both crystals, as far as the variation of S is concerned. If extinction is present, the scale factor should decrease with decreasing E, since stronger reflections are more seriously affected by extinction.

TABLE 4

	Number of reflections	Scale factor	E
Crystal A	100	2.215(9)	40.0
	98	2.213(10)	30.0
	95	2.201(10)	25.0
	91	2.204(11)	20.0
Crystal B	101	2.980(7)	40.0
	99	2.971(8)	30.0
	96	2.972(9)	25.0
	93	2.975(10)	20.0

Based on the latter argument and on the results shown in Table 4, five reflections from crystal A with $|F_{calc}| > 25$ and four reflections from crystal B with $|F_{calc}| > 26$ were excluded from the final cycles of the refinement.

A Fourier refinement was carried out based on the observed structure factors wheighed according to the inverse of the corresponding Poisson variance, $\sigma_F^2 = (\sigma_I/2F)^2$.

The data sets for both crystals were finally scaled together, using the appropriate scale factors obtained in the last cycle of the structure refinement.

5 — DISCUSSION

The above results show that the 154 independent reflection intensities from crystal A do not deviate significantly from a Poisson distribution with $v = 1.20$ and $R = 0.023$ (Table 1). However, similar data from crystal B, significantly deviate from this distribution, as evidenced by the larger value of $v = 1.54$; the large R-factor, $R = 0.031$, obtained from this data set is probably due to the smaller sample size, since only 54 independent observations were available in this case.

The above deviation from Poisson statistics can be understood taking into account the much smaller value of γ used for the data collection from crystal B (Table 1). Intensities from this crystal were measured for a very long time; as a consequence, the corresponding Poisson variances become unrealistically smaller than typical instrumental variances, such as time drifts and inhomogeneity of the primary beam. Therefore, the question of increasing the reliability of the data by spending more time measuring the integrated intensities arises and should be discussed. This will be postponed until more experience is gained concerning such long time measurements.

As far as the crystallographic R-factors are concerned (see Table 5) it appears in the present work that the quality of the data improves as the time spent in each measurement is increased.

TABLE 5

Crystal	N.º of independent reflections	N.º of parameters refined	Crystallographic R – factors		Goodness of fit
			R-weighed	R	
A	95	8	0.020	0.023	2.3
B	96	8	0.012	0.021	2.7
A + B	191	9	0.014	0.021	2.6

The goodness of fit (g.o.f.) parameters shown in Table 5 for both crystals are significantly different from unity. There is evidence that this is not caused by inaccuracy of the data or improper standard deviations: out of the reflections which are common to both crystals, there are eleven from crystal A which have $|F_{obs}-F_{calc}| > 2\,\sigma_F$; of these, only in four cases does the above difference change sign when taken for crystal B. Similarly, taking the nineteen reflections common to both crystals which, for crystal B, yield $|F_{obs}-F_{calc}| > 2\,\sigma_F$, only five behave as mentioned above.

The values obtained for the above parameters indicate that the model assumed in the course of the present refinement deviates from the observed one. Such deviation may be due to the fact that neither thermal diffuse scattering, nor anharmonic motion have been taken into account; but the most significant deviation probably arises from the fact that the electron density in this compound is not spherically symmetric, as was assumed for the calculation of structure factors.

The work on this compound is to be continued with the aim of investigating the electron density distribution.

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