CONTRIBUTION TO THE STUDY OF THE ELECTRON DISTRIBUTION IN VF_2 (*)

M. M. R. COSTA and M. J. M. DE ALMEIDA
Centro FC1, INIC — Departamento de Física, Universidade de Coimbra
3000 Coimbra, Portugal

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ABSTRACT — A contribution to the study of the electron density distribution in VF_2 is given in the present paper.

A set of observed X-ray intensities from a single crystal were placed on the same scale as corresponding values calculated for a postulated model; the scale factor was obtained from least-squares refinement of high order data ($0.6\ \text{Å}^{-1} < (\sin\theta)/\lambda < 1.1\ \text{Å}^{-1}$).

Fourier difference maps are shown for different sections through the unit cell.

1 — INTRODUCTION

The compound VF_2 has been synthesized by Stout and Boo [1]. These authors have investigated its heat capacity in the temperature range 5-300 K as well as the magnetic interactions responsible for the magnetic ordering in the compound. More recently, the crystal distortion associated with magnetic ordering has been studied by Mc-Cain et al. [2] who measured the lattice parameters of single crystals of VF_2 at different temperatures ranging from 4.2 K to 298 K.

Statistical tests on the X-ray diffraction data together with a study of the crystal structure and anisotropic thermal parameters of single crystals of VF_2 have been carried out by Almeida et al. [3].

The present study represents a further contribution leading to the determination of the electron densities in that compound in order to investigate possible asphericities in the electron distributions.

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2 — DATA COLLECTION

VF_2 has a rutile type structure with space group $P4_2/mnm$ (Stout and Boo) [4].

A single crystal of VF_2 with approximate dimensions $(0.04 \times 0.05 \times 0.10)\,mm^3$ obtained from a large specimen grown by B. J. Garrard, Clarendon Laboratory, Oxford (England) was used in the present study.

The lattice parameters have been determined as described elsewhere [3].

$$a = b = (4.803 \pm 0.005)\ \text{Å}\ ;\ c = (3.235 \pm 0.005)\ \text{Å}$$

Several $\omega - 2\theta$ scans were carried out to measure the integrated intensities of 1177 reflections out to $(\sin\theta)/\lambda = 1.1\ \text{Å}^{-1}$ on a CAD4 four-circle diffractometer using Mo-Kα radiation and a graphite monochromator. For each hkl, between two and sixteen equivalent reflections were collected to enable a study of absorption and extinction in this crystal. The intensities of three reflections were periodically measured and used as standards against which all reflection intensities were calibrated.

3 — DATA REDUCTION

Lorentz and polarization corrections were applied to the measured integrated intensities $I_{hkl} > 3\,\sigma_{hkl}$, where σ_{hkl} is the standard deviation of the intensity I_{hkl}.

An empirical absorption correction described by North et al [5] based on the method proposed by Furnas [6] was applied in an attempt to improve the agreement between equivalent reflections.

The calculated transmission factors varied between 0.946 and 0.998. For each group of equivalent reflections, thus corrected for absorption, agreement factors were calculated as:

$$R = \sum_{hkl} |\, F_{hkl} - F_{av} \,| \,/\, \left(\sum_{hkl} F_{hkl} \right)$$

$$R' = \left\{ \sum_{hkl} |\, F_{hkl} - F_{av} \,|^2 \,/\, \left(\sum_{hkl} F^2_{hkl} \right) \right\}^{1/2}$$

where F_{av} represents the average of the structure amplitudes of a group of $\{ hkl \}$ equivalent reflections. For most reflections the values of R and R′ were of the order of 1 % and 2 % respectively; only for six reflections both R and R′ varied between 2 % and 5 %.

Within each group of equivalent reflections, those for which $|F_{hkl} - F_{av}| > 3\,\sigma_{hkl}$ were rejected: the remainder were used to calculate a new value of F_{av} which was used in all subsequent calculations.

A set of structure amplitudes, F_c, were calculated on the assumption of spherical distributions of electrons around the nuclei of vanadium and fluorine atoms: the atomic scattering factors for the ionized spherical atoms were obtained from the constants a_i, b_i ($i = 1, 3$) and c listed on the International Tables for X-ray Crystallography (vol. IV); anomalous dispersion corrections for Mo - Kα radiation were included.

A least squares refinement (hereafter referred to as refinement (i)) was carried out including all 113 reflections with $0.1\ \text{Å}^{-1} < (\sin\theta)/\lambda < 1.1\ \text{Å}^{-1}$. The results obtained for the anisotropic thermal parameters and position of the fluorine atom agree with those given elsewhere [3] for this structure. They are shown in the table together with the value of the scale factor. The observed structure amplitudes multiplied by the scale factor were then plotted against the corresponding F_c. The significant deviation from the straight line of the two points representing the 110 and the 002 reflections indicated the presence of extinction affecting these intensities.

A further refinement of the above mentioned parameters based on all but these two reflections was performed, yielding refined values in good agreement with those previously obtained.

In order to bring the experimental intensities on an absolute scale, a direct measurement of the scale factor, S, would be desirable. It is reasonable to expect that this will differ significantly from the value yielded by a refinement which includes reflections with low $(\sin\theta)/\lambda$: in fact any deviation of the real electron density from the postulated spherical model is likely to modify the calculated intensities of such reflections; moreover, these low angle reflections, having usually the highest intensities, are the most significantly affected by extinction. These two effects add up to mask the "true" value of the scale factor.

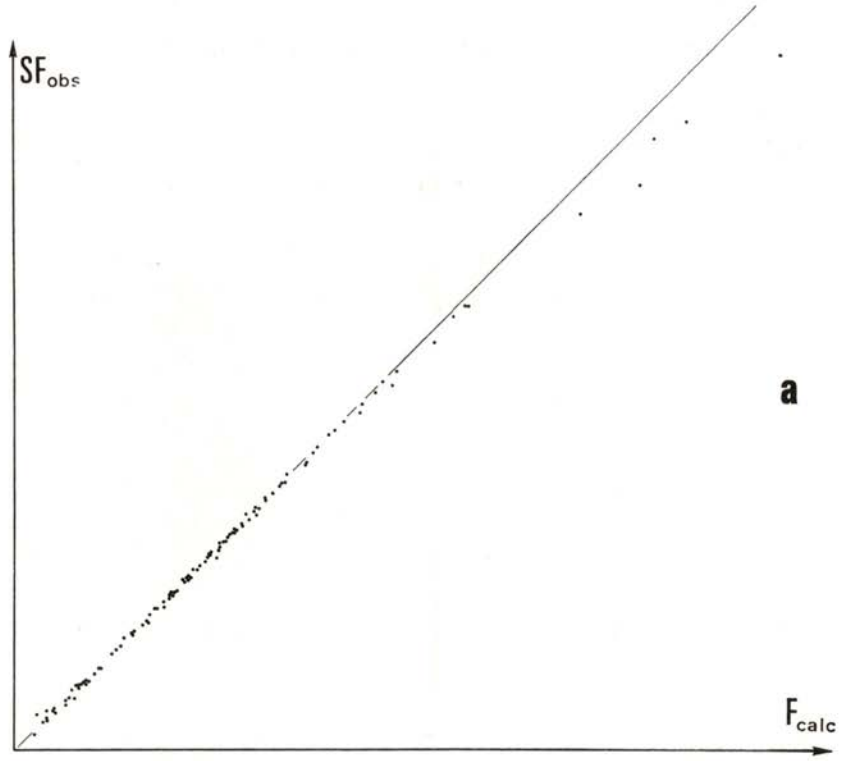
However, it has been pointed out by Stevens and Coppens [7] that a refinement of positional and thermal parameters based on higher order X-ray data usually yields a scale factor in good agreement with experimental values.

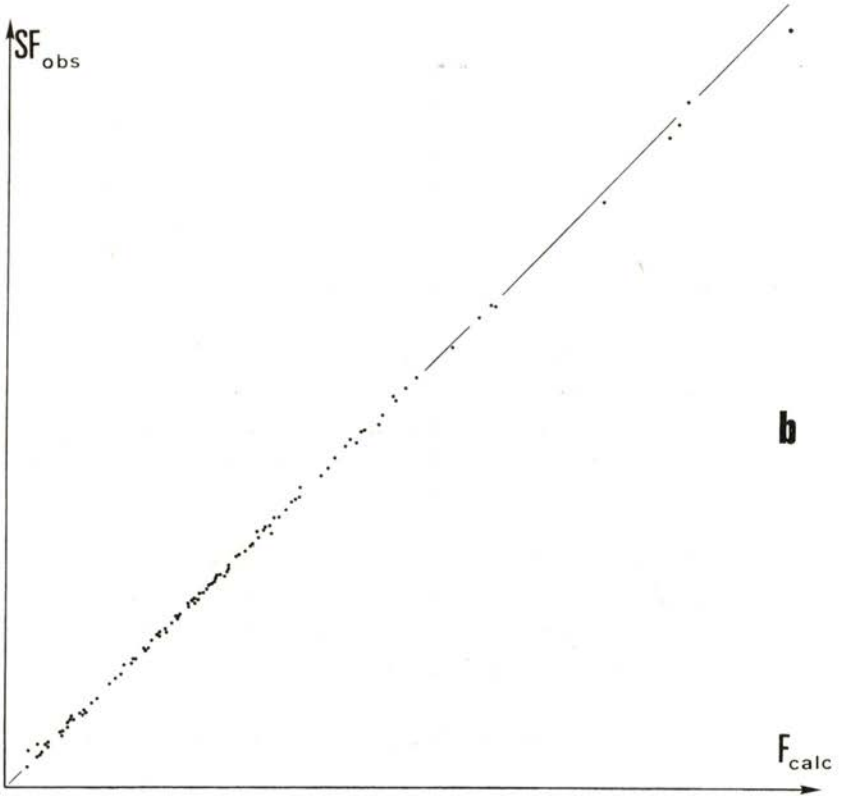
On the basis of such arguments a refinement based on only 68 reflections with 0.6 $Å^{-1} < (\sin\theta)/\lambda < 1.1$ $Å^{-1}$ was considered to be more correct; the results of this refinement (hereafter referred as refinement (ii)), also shown in the table, are to be compared with those obtained from the refinement of low and high order data. It may be seen that only the values of the scale factor are significantly different, as one would expect. The values of SF_o are plotted against the corresponding F_c in Fig. 1-a, which evidences the presence of extinction.

	Refinement (i)		Refinement (ii)	
	V	F	V	F
u_{11}	0.0058±0.0002	0.0116±0.0009	0.0063±0.0008	0.0127±0.0002
u_{33}	0.0049±0.0003	0.0077±0.0004	0.0054±0.0001	0.0085±0.0003
u_{12}	-0.0002±0.0003	-0.0053±0.0005	-0.0002±0.0001	-0.0057±0.0005
x	——	0.3048±0.0005	——	0.3050±0.0003
S	0.150±0.002		0.140±0.003	
R	0.018		0.014	
R_w	0.023		0.021	
g	——		$(0.93\pm0.06)\times10^{-5}$	

An attempt to correct the extinction effect was made, multipliying the calculated structure factors, F_c, by $(1 + gI_c)^{-1}$ where I_c is the calculated intensity and g an extinction parameter; the refinement of g was carried out keeping all thermal and positional parameters fixed at the values given by refinement (ii). Values of SF_o, thus corrected for extinction, are plotted in Fig. 1-b against the corresponding F_c; comparison with Fig. 1-a shows the extent to which the extinction effect has been corrected.

Fig. 1 (facing page) — (a) Plot of SF_o against F_c, before the extinction correction. (b) Plot of SF_o against F_c, when an extinction correction is applied to the observed structure amplitudes.


SF obs
a
F calc


SF obs
b
F calc

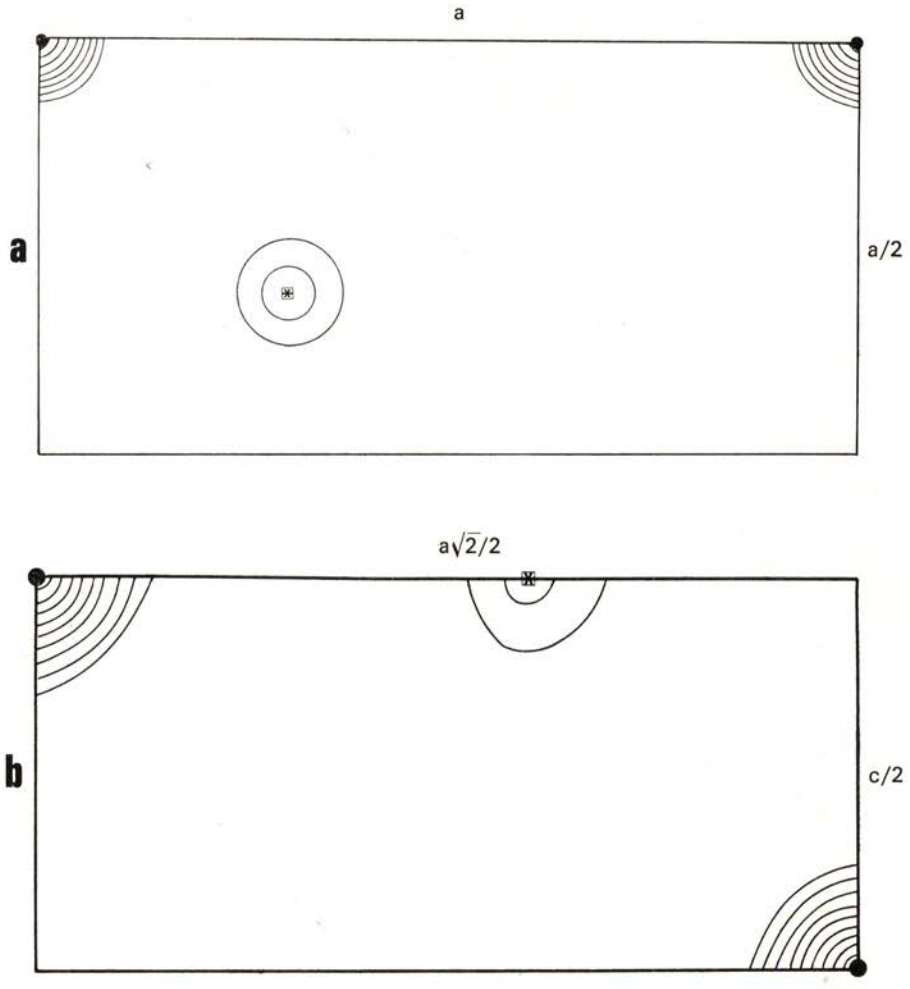


Fig. 2 — Fourier map of the observed structure amplitudes, SF_o.
● : position of V atoms; □ : position of F atoms.
(a) Section [001] of the unit cell.
(b) Section [1$\bar{1}$0] of the unit cell.

Fourier analyses of the observed (scaled) structure amplitudes, SF_o, and of the differences ($SF_o - F_c$) have been carried out. The corresponding density maps through different sections of the unit cell are shown in Figs. 2 and 3.

In all maps the curves away from the atomic positions are above the significance level. This was estimated by performing a Fourier analysis of the standard deviations of the observed data and drawing the corresponding density maps, shown in Fig. 4.

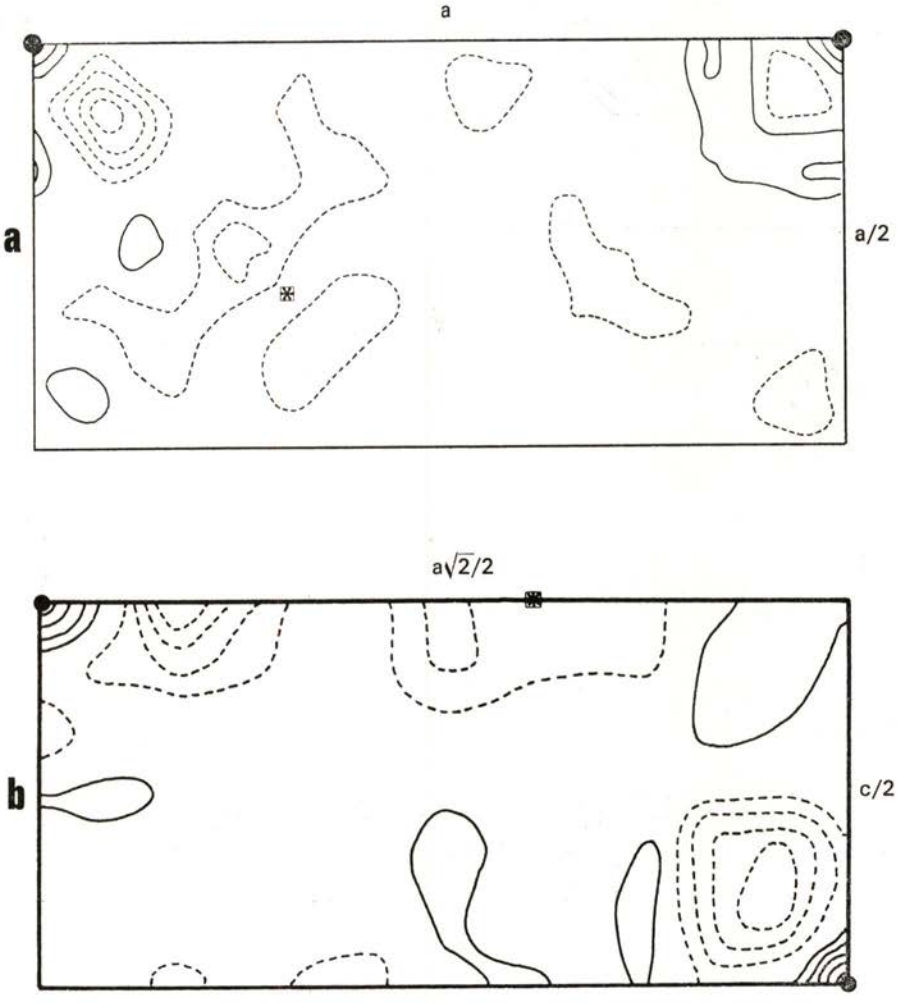


Fig. 3 — Fourier difference map, $SF_o - F_c$. Contours at 1/30 those of SF_o. Broken lines represent negative contours.

(a) Section [001] of the unit cell.

(b) Section [1$\bar{1}$0] of the unit cell.

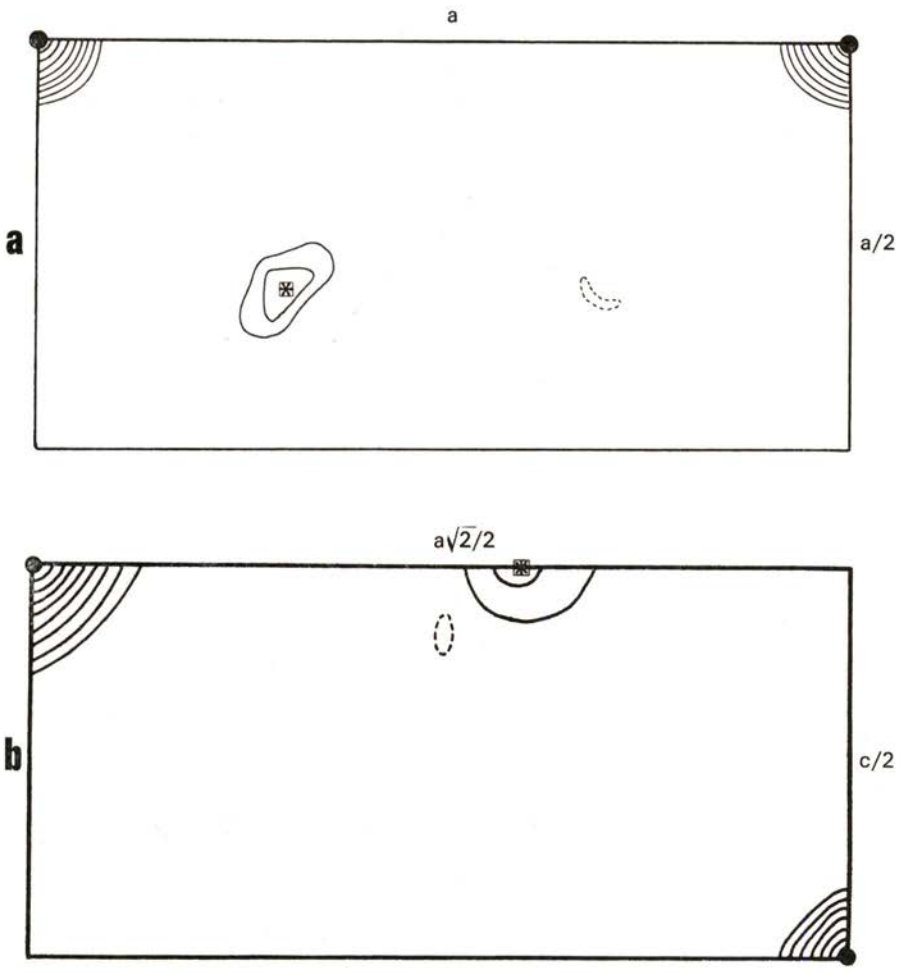


Fig. 4 — Fourier map representing the distribution of the errors in the unit cell. Contours at 1/30 those of SF_o.

(a) Section [001] of the unit cell.

(b) Section [1$\bar{1}$0] of the unit cell.

4 — DISCUSSION

A meaningful interpretation of the present results requires a direct measurement of the absolute scale, as was pointed out above; experiments leading to its determination are planned and will be carried out soon.

Comparison of Figs. 3 and 4 shows that the difference between the postulated spherical distribution of electrons in both V^{2+} and F^- ions and the real electron distribution, although rather small, is above the significance level. The possibility that the results are masked by extinction is to be taken into account, even though an extinction correction has been applied to the measured intensities. This suggests the convenience of collecting similar X-ray data from another crystal where the effect of extinction is greatly reduced; a nearly-extinction-free crystal has alread been selected and the results obtained will be compared with those of the present work.

It follows from the above arguments that definite conclusions concerning the electron density distribution in VF_2 cannot yet be drawn. However, it appears that the Fourier difference maps (Fig. 3) indicate a deficiency of electrons in the bonding directions, V - F .

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