# CHARGE DENSITY STUDY OF $VF_2$

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*(Received 16 October 1985)*

*ABSTRACT* — X-ray diffraction data from two single crystals of $VF_2$, obtained with two different wavelength radiations, Ag-K$\alpha$ and Mo-K$\alpha$, are compared in this paper.

The corrections applied to the observed data and the reproducibility of the results are analysed. The main features of the electron density in this compound are discussed in terms of Fourier difference maps.

## 1 — INTRODUCTION

The study of rutile type structures has been undertaken in our Laboratory in order to investigate the main features of the electron density of these compounds.

Previous results of X-ray diffraction from a single crystal of $VF_2$ (crystal I) at room temperature have already been reported [1]. These were based on intensity data collected on a CAD4 diffractomer at the Enraf-Nonius, Delft, using Mo-K$\alpha$ radiation. In order to test the reproducibility of these results, the data collection was repeated in our Laboratory under identical conditions, using the same crystal and the same type of radiation.

The corrections applied to the observed data were those described in reference [1]. Position and temperature parameters (Table 1) were refined from a set of 190 independent reflection intensities, using a least-squares technique. Comparison with similar parameters obtained from the previous data set showed that:

i) the position of the fluorine atom agrees within the experimental error;

ii) the anisotropic temperature parameters agree within 2 standard deviations;

iii) difference Fourier maps, $(\rho_{obs} - \rho_{calc})$, evidence similar features.

Similar experiments were carried out on a second crystal (II) with different dimensions; in this case, two wavelengths were used, in order to investigate the extinction effects, as will be discussed.

## 2 – DATA COLLECTION

A single crystal of $VF_2$ (cristal II) with prismatic shape and approximate dimensions ( $0.06 \times 0.07 \times 0.12$ ) $mm^3$ was selected from a large single crystal (from which specimen I had been cut) and used in the present work.

The lattice parameters were determined using the standard technique developped for X-ray diffractometry, as:

$$a = b = (4.806 \pm 0.010)\ \text{Å}\ ,\quad c = (3.237 \pm 0.007)\ \text{Å}\ .$$

Two independent experiments ( A and B ) were performed on a CAD4 four-circle diffractometer using Ag-K$\alpha$ and Mo-K$\alpha$ radiations, respectively. This was suggested by a comparison of data obtained from crystals I and II: no evidence for extinction was found when Ag-K$\alpha$ radiation was diffracted by crystal II; however, when crystal I, which is significantly smaller ([1]), was irradiated with a longer wavelength radiation ( Mo-K$\alpha$ ), some degree of extinction was detected as will be mentioned later.

Experiment B ( Mo-K$\alpha$ ) was hence carried out as an attempt to decide whether this effect should be attributed to the difference in wavelength of the incident beam or to a distinct mosaic spread in crystals I and II.

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([1]) The volume ratio for both crystals is $V_{II} / V_I = 2.5$.

Integrated intensities of reflections out to $(\sin\Theta)/\lambda = 1.02$ Å$^{-1}$ in experiment A and $(\sin\Theta)/\lambda = 1.08$ Å$^{-1}$ in experiment B were measured in $\omega - 2\Theta$ scans. Each reflection hkl was considered to be "observed" only if the corresponding integrated intensity, $I_{hkl}$, was such that $I_{hkl} > 3\,\sigma_{hkl}$, $\sigma_{hkl}$ being the standard deviation of $I_{hkl}$.

For each hkl, up to 16 symmetry-equivalent reflections were measured in order to correct for absorption of the beam inside the crystal.

A set of 1361 reflections were observed in experiment A and 1895 in experiment B. These will be referred to as sets A and B, respectively.

A few reflection intensities (five in experiment A and eight in B) were periodically measured and used as a standard against which all the other intensities were checked.

A plot of the standard intensities against time of measurement showed that their variation was in all cases smaller than 0.03 %.

## 3 – DATA ANALYSIS

Integrated intensities in sets A and B were corrected in the usual way for Lorentz and polarization effects [1]. Two different absorption corrections were calculated:

i) one which is based on the observed shape of the crystal from which the pathlengths of the incident and diffracted beams inside the crystal are derived;

ii) an empirical correction suggested by North et al. [2], which is based on the intensity variation for a few reflections occurring at high $\chi$-angles ($70° < \chi < 90°$) when the crystal is rotated around the scattering vector.

The latter method was found to yield the best agreement between the intensities of equivalent reflections; hence, the empirical absorption correction was applied to the data in both sets.

Least squares refinements including the 143 independent reflections of set A and 212 of set B were carried out. A plot

of the calculated structure factors against the observed ones placed on the same scale (Fig. 1 a)) showed that a few reflections

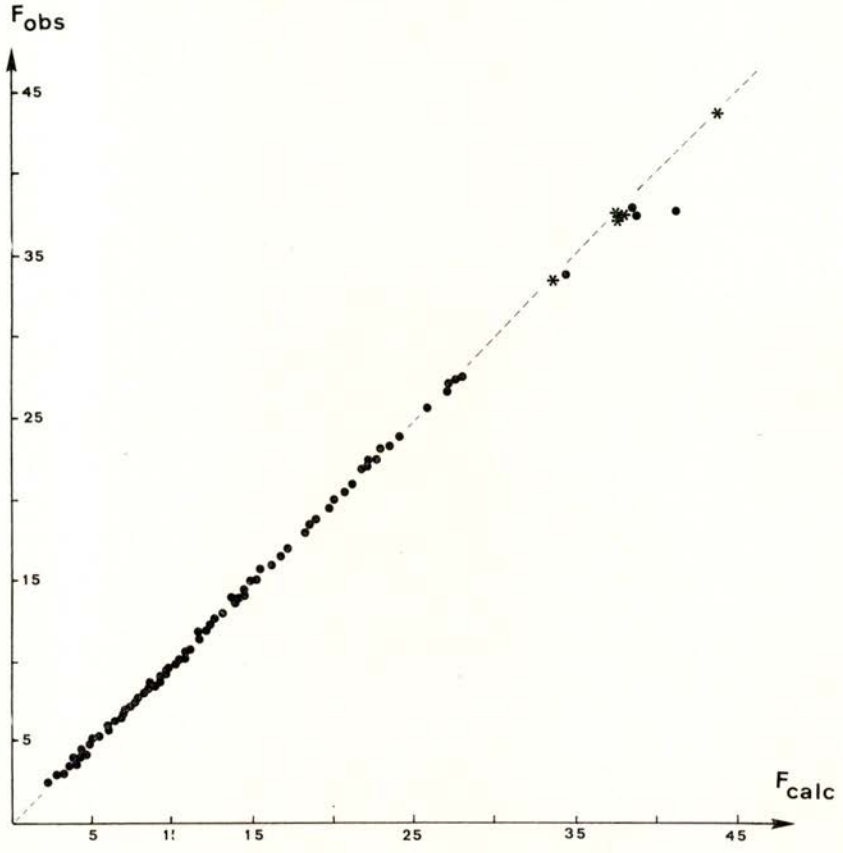


Fig. 1 a) — Plot of $SF_o$ against $F_c$ for crystal II (Mo-K$\alpha$ radiation)

- before the extinction correction

* when an extinction correction is applied (only reflections significantly affected by extinction are represented)

of data set B were affected by extinction; this is indicated by the deviation of the curve from a straight line.

No evidence for extinction was found in data set A (Fig. 1 b)). An extinction parameter was hence included in the refinement carried out for set B and the corresponding correction applied to these data.

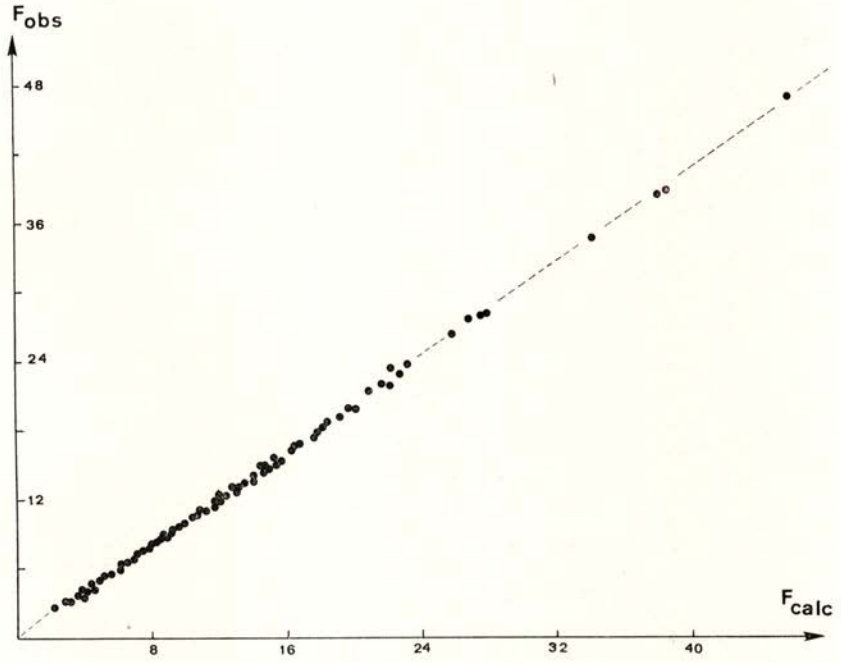


Fig. 1 b) — Plot of $SF_o$ against $F_c$ for crystal II (Ag-K$\alpha$ radiation)

According to Stevens and Coppens [3] a refinement based on high order reflection data should yield a more reliable value for the scale factor, S. In fact the low angle reflections are the most likely to be affected by extinction and asphericity in the electron distribution; therefore, their inclusion in a refinement is liable to mask the results.

Hence, a second refinement was carried out, based on reflections with $(\sin\theta)/\lambda > 0.6$ Å$^{-1}$, already corrected for extinction. The results are shown in Table 1; the scale factors can be compared

with those obtained from a refinement including all the reflections, namely:

$$S_I\,(\text{Mo-K}\alpha) = 0.1924(7)\ ,\ S_{II}\,(\text{Ag-K}\alpha) = 0.2124(8)\ ,$$
$$S_{II}\,(\text{Mo-K}\alpha) = 0.1007(7)$$

TABLE 1

| Parameter | Crystal I ( Mo-Kα ) | Crystal II ( Mo-Kα ) | Crystal II ( Ag-Kα ) |
|---|---|---|---|
| Atom: V | | | |
| $\beta_{11} = \beta_{22}$ | 0.00549 (3) | 0.00528 (2) | 0.00565 (4) |
| $\beta_{33}$ | 0.01073 (11) | 0.01001 (10) | 0.01037 (17) |
| $\beta_{12}$ | -0.00005 (4) | -0.00065 (12) | -0.00076 (28) |
| Atom: F | | | |
| x | 0.30509 (15) | 0.30533 (10) | 0.30536 (20) |
| $\beta_{11} = \beta_{22}$ | 0.01054 (14) | 0.01038 (9) | 0.01088 (16) |
| $\beta_{33}$ | 0.01609 (48) | 0.01522 (32) | 0.01397 (46) |
| $\beta_{12}$ | -0.00993 (44) | -0.00961 (38) | -0.00965 (59) |
| g | $(1.12 \pm 1.05) \times 10^{-5}$ | $(0.955 \pm 0.144) \times 10^{-6}$ | |
| S | 0.1936 (7) | 0.0998 (5) | 0.2174 (10) |
| R | 0.014 | 0.007 | 0.017 |
| $R_w$ | 0.015 | 0.012 | 0.023 |

An attempt was also made to measure the absolute scale experimentally. It is well known that the integrated intensity of any reflection ( $E_\omega$ ) is related to the absolute value of the corresponding structure factor, $F_{abs}$ :

$$(E_\omega) = S\,|F_{abs}|^2$$

where

$$S = I_0\,N^2\,\lambda^3\left(\frac{e^2}{mc^2}\right)^2 V_c$$

where $I_0$ is the intensity of the primary beam, N the number of unit cells per unit volume, $\lambda$ the wavelength of the incident radiation, $V_c$ the volume of the crystal used in the experiment and the remaining symbols have their usual meaning.

The measurement of $I_0$ was carried out using a method developped in our Laboratory [4] in which the use of absorbers is avoided; the dead time of the detector was measured and the corresponding correction applied to $I_0$.

Values of 0.2310 and 0.09675 were obtained for sets A and B, respectively. The estimated accuracy in S is of the order of 4 %; the main source of error (which may have been overestimated) is the determination of the crystal volume, $V_c$. This was calculated by careful observation of its shape and measurement of the length of its edges under a powerful microscope. The origin of the error in $I_0$ ( ~ 1 % ) is the unhomogeneity of the beam in the region occupied by the crystal; the dead time of the counter was measured with a precision better than 2 %.

In either case the experimental value of S was found to be closer to the value obtained from refinement of high order data.

Final structure factors ( $F_{calc}$ ) were calculated for reflections in sets A and B, using the parameters obtained from the latter refinement and assuming spherical distributions of the atomic electrons.

## 4 – FOURIER DIFFERENCE MAPS

Fourier analysis of the differences ( $S F_{obs} - F_{calc}$ ) enabled difference density maps to be drawn for two sections of the unit cell, namely [001] and [1$\bar{1}$0]. These are shown on Figs. 2 a), b) and 4 a), b) for crystal II and on Figs. 6 a), b) for crystal I. The results of Fourier syntheses of the corresponding standard deviations can be seen in Figs. 3, 5 and 7, which show that the error is only significant at or near the atomic sites. On each map one curve corresponds to 0.17 e/Å$^3$.

A few significant features can be observed in all maps:

i) a positive density near the vanadium sites along the directions joining two vanadium atoms (which are second nearest neighbours) on the z = 0 plane;

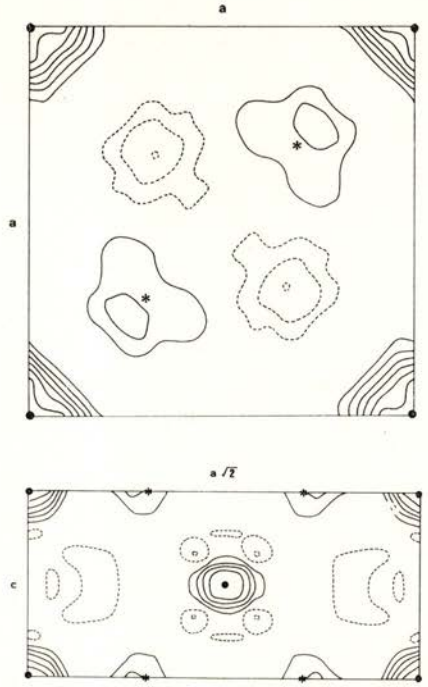


Fig. 2 a) e b)

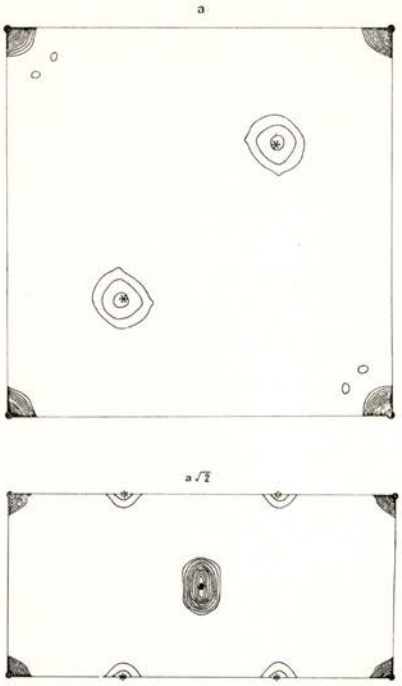


Fig. 3 a) e b)

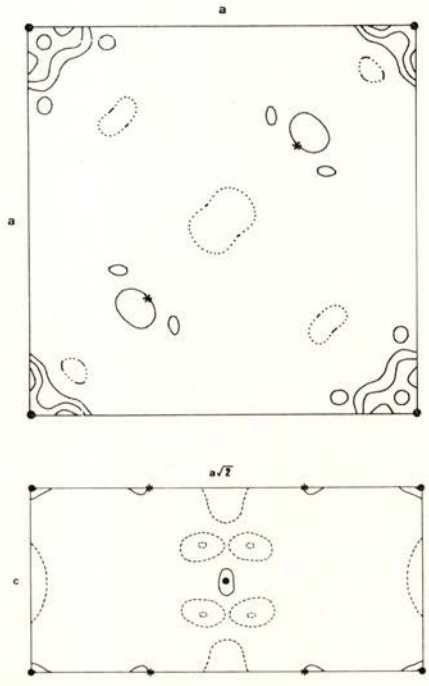


Fig. 4 a) e b)

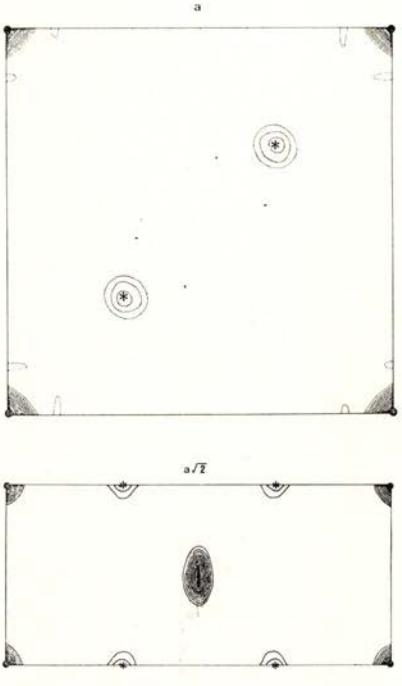


Fig. 5 a) e b)

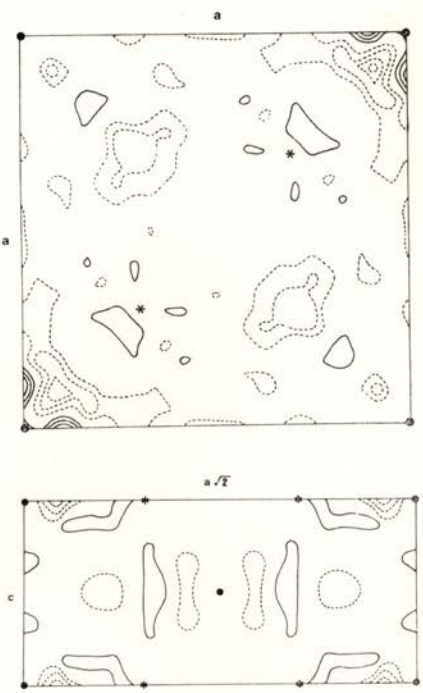


Fig. 6 a) e b)

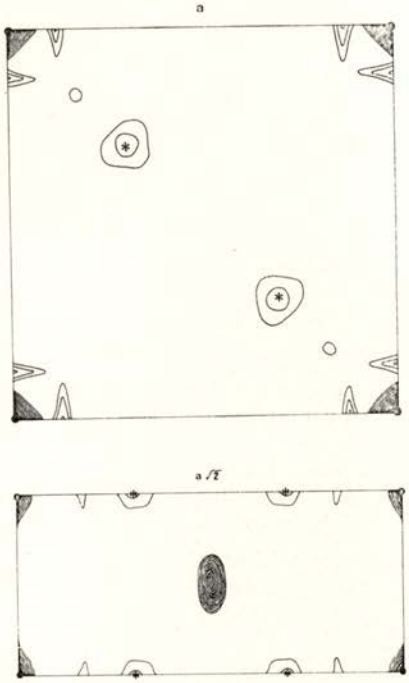


Fig. 7 a) e b)

Fig. 2 — Fourier difference maps, $SF_o - F_c$, for crystal II (Ag-K$\alpha$ radiation). Contour levels at 0.17 e/Å$^3$. Broken lines represent negative contours.
• : 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

Fig. 3 — Fourier maps representing the distribution of errors, for crystal II (Ag-K$\alpha$ radiation). Contour levels at 0.17 e/Å$^3$.
a) Section [001] of the unit cell; b) Section [1$\bar{1}$0] of the unit cell

Fig. 4 — Fourier difference maps, $SF_o - F_c$, for crystal II (Mo-K$\alpha$ radiation). Contour levels at 0.17 e/Å$^3$.
• : 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

Fig. 5 — Fourier maps representing the distribution of errors, for crystal II (Mo-K$\alpha$ radiation). Contour levels at 0.17 e/Å$^3$.
a) Section [001] of the unit cell; b) Section [1$\bar{1}$0] of the unit cell

Fig. 6 — Fourier difference maps, $SF_o - F_c$, for crystal I (Mo-K$\alpha$ radiation). Contour levels at 0.17 e/Å$^3$.
• : 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

Fig. 7 — Fourier maps representing the distribution of errors, for crystal I (Mo-K$\alpha$ radiation). Contour levels at 0.17 e/Å$^3$.
a) Section [001] of the unit cell; b) Section [1$\bar{1}$0] of the unit cell

ii) a positive density near the fluorine sites delocalised towards the vanadium atom;

iii) a negative density across the line joining the vanadium atom at the center of the unit cell and the fluorine atoms on the XY planes above and below.

Assuming that only the 3 d electrons of the transition element contribute to the observed difference densities, $\rho_{obs} - \rho_{calc}$, an attempt will be made to deduce from these the degree of asphericity in the distribution of such electrons.

We are indebted to the Cultural Service of the German Federal Republic Embassy, the Deutscher Akademischer Austauschdienst ( DAAD ) and the German Agency for Technical Cooperation ( GTZ ) for their interest that made possible the offer of a CAD4 automatic diffractometer used for the experiments described in the present work.

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