that the bright spots in the image do not correspond exactly to the positions of O atoms in the crystal. A similar shift of bright-spot images has already been observed in GaAs and AuAl (Hashimoto, Endoh, Takai, Tomita & Yokota, 1978–79) and in Si (Izui, Furuno & Otsu, 1977) and attributed to dynamic scattering of electrons in crystals and image formation with a limited number of waves (Krivanek & Rez, 1980). Similar comparisons and conclusions can also be made in the case of Cu_4O-S_2 as shown in Figs. 5(*a*)-(*c*). From these observations, it can be concluded that the suggested models are correct.

5. Discussion and concluding remarks

Two superstructures with the same chemical composition as Cu_4O, called Cu_4O-S_1 and Cu_4O-S_2, have been observed by HREM. In contrast to the structure of Cu_4O, a fraction of the O atoms in both Cu_4O-S_1 and Cu_4O-S_2 occupies the octahedral positions of the f.c.c. lattice of Cu. Since the space of the octahedra is larger than that of tetrahedra, it is possible that during the initial oxidation of Cu the O atoms may prefer to occupy first the octahedral sites then go to the tetrahedral sites to reduce the elastic interaction energy, until a uniform and perhaps more stable suboxide Cu_4O is formed. A similar phenomenon has been observed by Holley, Mulford, Ellinger, Kochler & Zachariasen (1955) and Korst & Warf (1956) in the hydrogen absorption of rare-earth metals, where the H atoms first go to the octahedral site of the f.c.c. lattice before the tetrahedra are filled by the H atoms, as confirmed by neutron diffraction and the measurements of the electric resistance. The present observation of superstructure may be explained as the occurrence of the same phenomenon.

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Asphericity Effects in the Electron Density of VF_2

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Abstract

The study of rutile-type structures has been undertaken in order to investigate the main features of the electron density in these compounds. The results of X-ray diffraction experiments carried out on VF_2 have been published elsewhere [de Almeida & Costa (1985). *Port. Phys.* 16, 181-190]. Significant contour levels observed in difference Fourier maps were attributed to the asphericity of the 3*d*-electron distribution in the crystalline field of the rutile-type structure. Attempts were made to interpret these effects quantitatively by carrying out: (i) a fit of the parameters which represent the occupancy of each of the 3*d* orbitals, based on comparison of the observed structure factors with those calculated from 3*d* wave functions; (ii) a multipole refinement of the parameters which determine the occupation of the 3*d* orbitals in the crystal field. Crystal data: VF_2, $M_r = 88{\cdot}94$, tetragonal, $P4_2/mnm$, $a = 4{\cdot}806\,(10)$, $c = 3{\cdot}237\,(7)$ Å, $V = 74{\cdot}77$ Å^3, $Z = 2$, $D_x = 3{\cdot}945$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7017$ Å, $\lambda(\text{Ag } K\alpha) = 0{\cdot}5594$ Å, $\mu(\text{Mo } K\alpha) = 30{\cdot}3$ cm^{-1}, $\mu(\text{Ag } K\alpha) = 15{\cdot}2$ cm^{-1}, $F(000) = 82$, room temperature. Final R values for the Mo $K\alpha$ and Ag $K\alpha$ data were 0·014 for 190 reflections and 0·017 for 143 reflections, respectively.

Introduction

The study of rutile-type structures, MF_2, where M is a first-series transition metal, has been undertaken in our laboratory. The aim of this work is a careful determination of the electron-density distribution with a degree of accuracy which would enable a quantitative analysis of the charge-density asphericity

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to be carried out. This paper describes the results obtained for vanadium difluoride. A detailed discussion of the experimental conditions used in data collection and of data analysis, as reported in a previous paper (de Almeida & Costa, 1985), will be summarized in the following paragraphs.

An attempt was made to interpret in a quantitative way the effects observed on difference Fourier maps by carrying out a refinement of the parameters which define the occupancy of the $3d$ orbitals in the crystal field.

Data collection

Specimens I and II with approximate dimensions $0{\cdot}04\times0{\cdot}05\times0{\cdot}10$ mm and $0{\cdot}06\times0{\cdot}07\times0{\cdot}12$ mm respectively were cut from the same large single crystal, grown by B. J. Garrard, Clarendon Laboratory, Oxford (England) (Wanklyn, Garrard & Wondre, 1976). The lattice parameters were determined from 23 reflections with $37<2\theta<52°$ for crystal I and 25 reflections with $18<2\theta<63°$ for crystal II using the standard technique developed for X-ray diffractometry: $a=b=4{\cdot}806\,(10)$, $c=3{\cdot}237\,(7)$ Å. X-ray intensities diffracted by both crystals were measured on a CAD-4 four-circle diffractometer.

Two independent experiments, A and B, were performed: a set of 2447 integrated intensities from crystal II were observed and measured using Ag $K\alpha$ radiation in experiment A. A similar set of data, consisting of 2882 reflection intensities from crystal I, were obtained in experiment B, using Mo $K\alpha$ radiation.

Reflections within a sphere of reciprocal space $(-10\le h\le 10,\ -10\le k\le 10,\ -6\le l\le 6)$ out to $(\sin\theta)/\lambda=1{\cdot}1$ Å^{-1} were measured in ω-2θ scans; those for which $I_{hkl}\le 3\sigma_{hkl}$, σ_{hkl} being the standard deviation of I_{hkl}, were considered to be 'unobserved' (1089 in set A and 987 in set B).

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

Five reflection intensities in experiment A and eight in experiment B were periodically measured and used as standards against which all the other intensities were checked. A plot of these intensities against time of measurement showed that their variation was in all cases smaller than 0·03%.

Data analysis

Data analysis was carried out using programs developed by Enraf-Nonius (*SDP-Plus*; Frenz, 1983) and a PDP 11-34 with RSX11M operating system. Lorentz and polarization corrections were applied in the usual way to the integrated intensities of sets A and B. An empirical absorption correction suggested by North, Phillips & Mathews (1968) was applied to the data (sets A and B). This method was preferred to that based on the calculation of the path lengths of the incident and diffracted beams inside the crystal, since it yielded a better agreement between the intensities of equivalent reflections.

Table 1. *Results of data refinement*

Parameter	Crystal I (Mo $K\alpha$)	Crystal II (Ag $K\alpha$)
Atom: V		
$\beta_{11}=\beta_{22}$	0·00549 (3)	0·00565 (4)
β_{33}	0·01073 (11)	0·01037 (17)
β_{12}	−0·00005 (4)	−0·00076 (28)
Atom: F		
x	0·30509 (15)	0·30536 (20)
$\beta_{11}=\beta_{22}$	0·01054 (14)	0·01088 (16)
β_{33}	0·01609 (48)	0·01397 (46)
β_{12}	−0·00993 (44)	−0·00965 (59)
g	$1{\cdot}12\,(1{\cdot}05)\times10^{-5}$	
S	0·1936 (7)	0·2174 (10)
R	0·014	0·017
wR	0·015	0·023

Maximum and minimum values of the correction were found to be 0·9988 and 0·9370 for crystal I (set B) and 0·9987 and 0·9412 for crystal II (set A). Agreement factors of 2·7 and 2·8% for equivalent reflections of sets A and B, respectively, were obtained. Full-matrix least-squares refinements including 143 independent reflections of set A and 190 of set B were carried out on F^2, using a non-Poisson contribution weighting scheme.

The quantities minimized were $(F_{\rm obs}-F_{\rm calc})^2$, $F_{\rm calc}$ being the structure factor calculated on the basis of a postulated structure (rutile type) and a spherical distribution of the atomic electrons. Anomalous-dispersion corrections were taken into account (*International Tables for X-ray Crystallography*, 1974). A plot of the calculated against the observed structure factors showed that a few strong reflections from crystal I (set B) were affected by extinction. No evidence for this effect was found in data set A.

Both extinction and asphericity in the electron distribution are likely to affect low-angle reflections far more seriously than high-angle ones. Their inclusion in a refinement is liable to mask the results. Hence, a refinement based only on high-order reflection data should yield a more reliable value for the absolute scale factor, S, as suggested by Stevens & Coppens (1975). The final shift/e.s.d. ratio was 0·0 for all parameters refined.

The results obtained from refinements of data with $(\sin\theta)/\lambda>0{\cdot}6$ Å^{-1} are shown in Table 1.*

The extinction parameter was refined independently. The scale factors can be compared with those obtained from refinements which included all the reflections, namely $S_{\rm I}({\rm Mo}\ K\alpha)=0{\cdot}1924\,(7)$,

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* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43856 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

S_{II}(Ag $K\alpha$) = 0·2124 (8). The absolute scale factor, S, was also measured experimentally, after experiment A. As is well known, this involves the measurement of the intensity I_0 of the primary beam, as well as an evaluation of the volume, V, of the crystal.

The measurement of I_0 was based on a method developed in our laboratory (Andrade, Costa & de Almeida, 1983). The dead time of the detector was measured and the corresponding correction applied to I_0. The value thus obtained for S was 0·2310; this is closer to the value obtained from a refinement of only high-order data, as expected. The estimated accuracy in S is not better than 4%; the main source of error (which may well have been overestimated) is the determination of the crystal volume, V. This was calculated by careful observation of its shape and dimensions under a powerful microscope. The origin of the error in I_0 ($\leq 1\%$) is the unhomogeneity of the main beam over the region occupied by the crystal. The dead time of the counter was measured with a precision better than 2%.

Final structure factors ($F_{\rm calc}$) were calculated for reflections in sets A and B, using the parameters listed in Table 1 and assuming spherical distributions of the atomic electrons.

Fourier analysis of each of the above-mentioned data sets enabled difference maps to be drawn for two sections of the unit cell. These are shown in Figs. 1(*a*), (*b*) and 3(*a*), (*b*); the corresponding error maps are represented in Figs. 2(*a*), (*b*) and 4(*a*), (*b*).

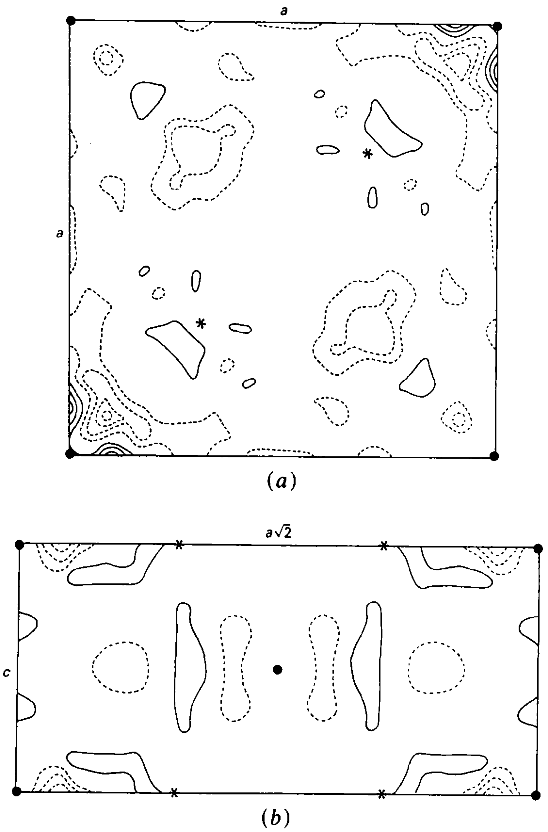
A few common features can be observed on these maps:

(i) on the $z = 0$ plane a positive deformation density near the V sites, along the direction joining two second-nearest neighbours and also near the F atom pointing towards a V atom;

(ii) on the (110) plane a negative deformation density along the direction joining two nearest neighbours (V and F).

These contour levels observed above the significance level were attributed to the asphericity of the 3d-electron distribution, arising from the symmetry of the crystalline field in vanadium difluoride.

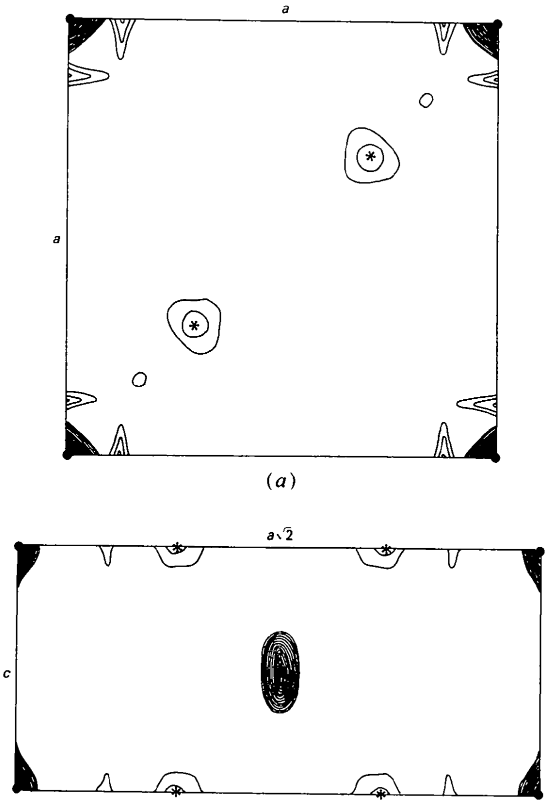
An attempt was made to interpret such effects in a quantitative way, by carrying out a refinement of the parameters which define the occupancy of the 3d orbitals in the crystal field.



(*a*)

(*b*)

Fig. 1. Difference Fourier maps of VF_2 (crystal I, Mo $K\alpha$ radiation). The contour interval is 0·17 e Å^{-3}; solid and dashed lines represent positive and negative contours, respectively. V atoms are indicated by ● and F atoms by ⁎. (*a*) [001] section; (*b*) [110] section.



(*a*)

(*b*)

Fig. 2. Fourier maps representing the distribution of errors in VF_2 (crystal I, Mo $K\alpha$ radiation). The contour interval is 0·17 e Å^{-3}. V atoms are indicated by ● and F atoms by ⁎. (*a*) [001] section; (*b*) [110] section.

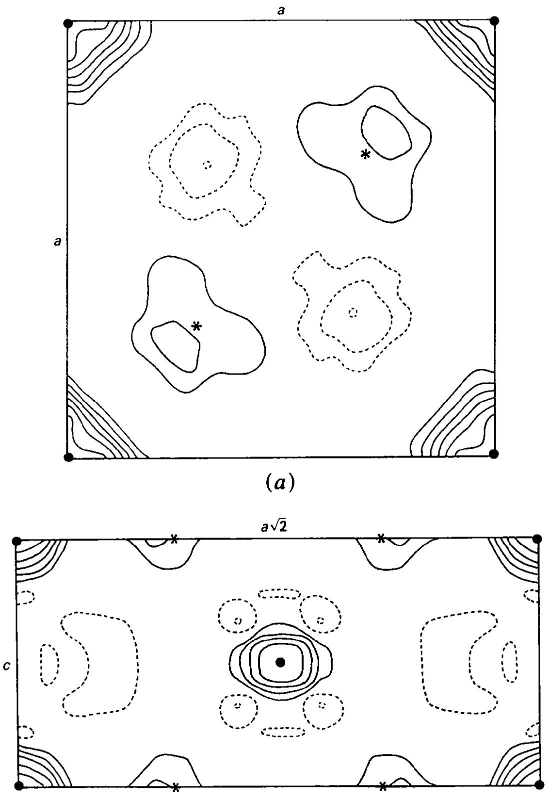
Analysis based on 3*d* wave functions

The shape and asphericities of the observed 3*d*-electron distribution in VF_2 can be analysed by comparison with the charge density deduced from the one-electron wave functions for the free V^{2+} ion.

The 3*d* electrons correspond to a fivefold-degenerate level ($L=2$) with wave functions d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz}, whose angular dependence, referred to the set of orthogonal axes *OXYZ* shown in Fig. 5, has been given by Abragham & Bleaney (1970). The symmetry of the crystal field determines whether the degeneracy of the corresponding levels is partially or totally lifted.

In the case of VF_2 the crystalline environment of the metal ion is such that the negative ions (F^-) occupy the corners of a slightly deformed octahedron. Hence, the crystal field has orthorhombic symmetry. The magnitude of the distortion, however, justifies the assumption of tetragonal symmetry, which has been made throughout this work.

The five 3*d* orbitals will be denoted as e_{g_1}, e_{g_2}, t_{2g_1}, t_{2g_2} and t_{2g_3}, with wave functions d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz} and d_{yz}, respectively; t_{2g_2} and t_{2g_3} orbitals are equivalent by symmetry.

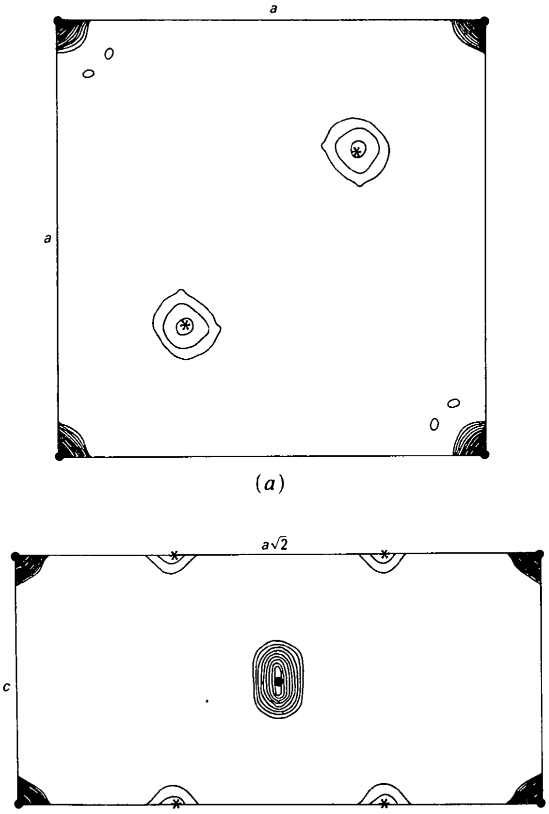


(*a*)

(*b*)

Fig. 3. Difference Fourier maps of VF_2 (crystal II, Ag *Kα* radiation). The contour interval is $0{\cdot}17$ e Å^{-3}; solid and dashed lines represent positive and negative contours, respectively. V atoms are indicated by ● and F atoms by $\ast$. (*a*) [001] section; (*b*) [110] section.

The comparison of the calculated wave functions with those representing the symmetry of the electron distribution observed in VF_2 was performed in terms of structure factors. These were calculated as will now be described.



(*a*)

(*b*)

Fig. 4. Fourier maps representing the distribution of errors in VF_2 (crystal II, Ag *Kα* radiation). The contour interval is $0{\cdot}17$ e Å^{-3}. V atoms are indicated by ● and F atoms by $\ast$. (*a*) [001] section; (*b*) [110] section.

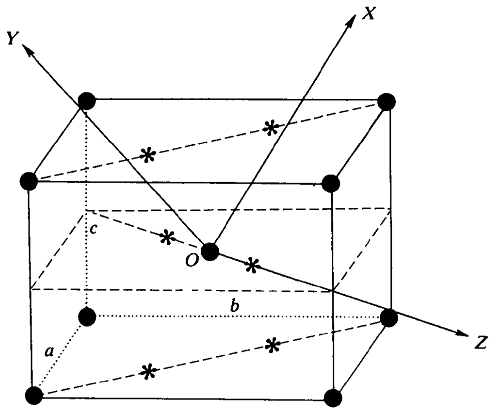


Fig. 5. Crystal structure of VF_2. *OXYZ* is the set of axes used in the quantitative analysis of asphericities; *a*, *b*, *c* indicate the directions of crystallographic axes.

The scattering factor, $f(\mathbf{K})$, for a particular reflection is

$$f(\mathbf{K})=\int \Psi^*(\mathbf{r}) \exp(i\mathbf{K}.\mathbf{r})\Psi(\mathbf{r})\,d^3r, \qquad (1)$$

where $\mathbf{K}$ is the scattering vector for that reflection and $\Psi(\mathbf{r})$ are the one-electron wave functions.

As was pointed out by Schweitzer (1980), $f(\mathbf{K})$ may be written

$$f(\mathbf{K})=\sum_H \langle j_H(K)\rangle\left[\sum_Q C_Q^H Y_Q^H(\theta,\varphi)\right], \qquad (2)$$

where the C_Q^H are the appropriate $3j$ Clebsh–Gordon coefficients (Condon & Shortley, 1963) and the integrals $\langle j_H(K)\rangle$ $(H=0,2,4)$ are defined in terms of spherical Bessel functions, $j_H(K,r)$, as

$$\langle j_H(K)\rangle=\int_0^\infty r^2 j_H(K,r)[R(r)]^2\,dr. \qquad (3)$$

From (2), with the scattering vector $\mathbf{K}$ referred to the set of axes $OXYZ$ shown in Fig. 5, together with the properties of the $3j$ coefficients, the scattering factor for each of the $3d$ orbitals can be derived.

Only the aspherical contributions to the scattering factor – the $\langle j_2\rangle$ and $\langle j_4\rangle$ terms above – have been taken into account. This is justifiable, because the charge density observed on the density maps (Figs. 1 and 2) represents the Fourier transform of the differences between the observed structure factors, SF_o, and those calculated on the basis of a spherical electron distribution associated with both ions ($F_{\rm calc}$). Hence, the differences ($SF_o - F_{\rm calc}$) were taken as the 'observed aspherical structure factors' (F_o^a) to be compared with similar quantities, $F_{\rm calc}^a$, calculated on the basis of the above model.

The total aspherical scattering factor, $f^a(\mathbf{K})$, was expressed as a linear combination of the contributions from each $3d$ orbital:

$$f^a(\mathbf{K})=\alpha_1 f^a_{e_{g_1}}+\alpha_2 f^a_{e_{g_2}}+\alpha_3 f^a_{t_{2g_1}}+\alpha_4 f^a_{t_{2g_2}}+\alpha_5 f^a_{t_{2g_3}},$$

α_i $(i=1,\ldots,5)$ being adjustable fractional parameters which define the occupancy of each orbital. The tetragonal symmetry assumed for the crystal field and the normalization condition impose two constraints on these parameters:

$$\alpha_4=\alpha_5 \qquad \alpha_5=[1-(\alpha_1+\alpha_2+\alpha_3)]/2.$$

A set of 'aspherical structure factors', $F^a(\mathbf{K})$, were then calculated in the usual way and compared with the corresponding observed structure factors. The scattering vector $\mathbf{K}$ and hence the indices hkl of the observed data were redefined, taking into account the relative orientation of the set of axes $OXYZ$ and the crystallographic axes in terms of which the observed h, k, l and hence $\mathbf{K}$ were defined (see Fig. 5).

Only the structure factors for which $F_{\rm calc}^a \neq 0$ and $(\sin\theta)/\lambda < 0{\cdot}6$ Å^{-1} were included in the refinement of the parameters α_i. These low-angle reflections are the most sensitive to the details of the charge-density distribution; moreover, higher-order reflection data are more likely to be affected by thermal effects, their accuracy being reduced by the uncertainty in the corrections.

Three parameters α_1, α_2 and α_3 were varied as shown in Figs. 6(*a*), (*b*), (*c*) and 7(*a*), (*b*), (*c*), for crystals I and II, respectively. The best fit to the observed structure factors was obtained for the values shown in Table 2.

Multipole analysis

An independent attempt to interpret the observed asphericities in the charge-density distribution of VF_2 was based on the multipole model proposed by Stewart (1973, 1976).

The wave functions used in the multipole expansion of the charge density about each atomic centre are products of a radial function for the lth-order multipole of atom p (R_{pl}) and a Tesseral

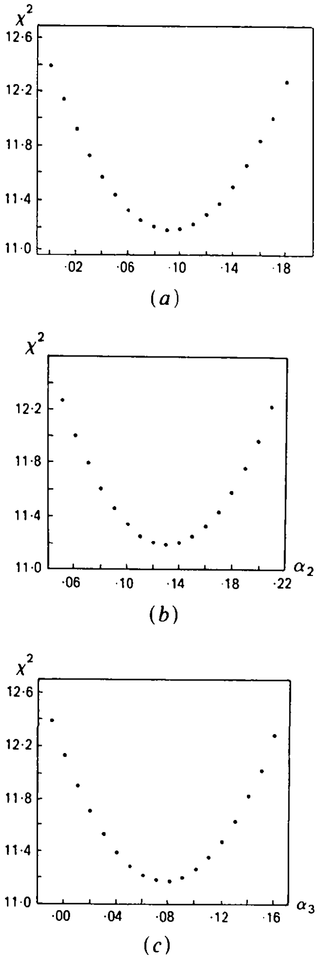


Fig. 6. (*a*) Variation of χ^2 with α_1 for crystal I; $\alpha_2=0{\cdot}13$; $\alpha_3=0{\cdot}08$. (*b*) Variation of χ^2 with α_2 for crystal I; $\alpha_1=0{\cdot}09$; $\alpha_3=0{\cdot}08$. (*c*) Variation of χ^2 with α_3 for crystal I; $\alpha_1=0{\cdot}09$; $\alpha_2=0{\cdot}13$.

harmonic $P_l^m(\cos\theta)\begin{cases}\cos(m\varphi)\\ \sin(m\phi)\end{cases}$; the latter are generated by orbital products among $2s$, $2p$ and $3d$ atomic orbitals on the same scattering centre.

The Fourier transform of such products is a basis for the representation of the atomic scattering factor.

Only multipoles which transform as the totally symmetric representations of the point group describing a particular site symmetry have to be taken into account.

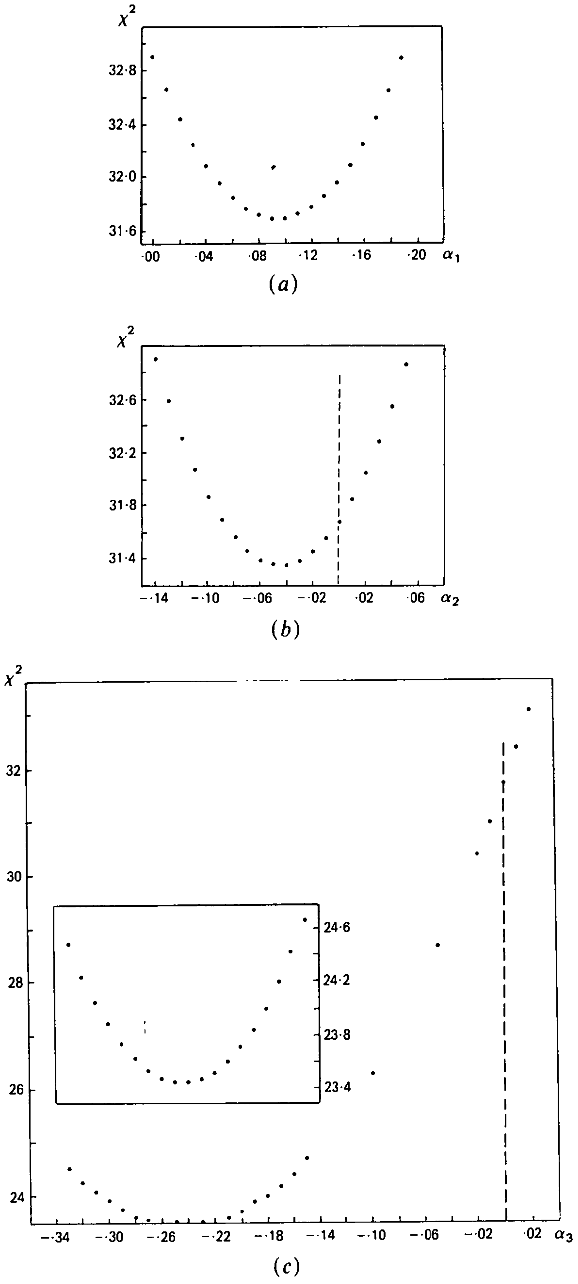


Fig. 7. (a) Variation of χ^2 with α_1 for crystal II; $\alpha_2=0{\cdot}00$; $\alpha_3=0{\cdot}00$. (b) Variation of χ^2 with α_2 for crystal II; $\alpha_1=0{\cdot}10$; $\alpha_3=0{\cdot}00$. (c) Variation of χ^2 with α_3 for crystal II; $\alpha_1=0{\cdot}10$; $\alpha_2=0{\cdot}00$. Inset: same variation on the scale of (a) and (b).

Table 2. *Results obtained by best fit to observed structure factors*

Parameters	α_1	α_2	α_3	$\alpha_4=\alpha_5$
Crystal I	0·09 (8)	0·13 (8)	0·08 (8)	0·35 (7)
Crystal II	0·10 (9)	0·00 (8)	0·00 (9)	0·46 (8)

The multipole basis functions compatible with the site symmetry of the V^{2+} ion in VF_2, mmm, include one monopole, P_0^0, two quadrupoles, P_2^0 and $P_2^2\begin{cases}\cos(2\varphi)\\ \sin(2\varphi)\end{cases}$ and three hexadecapoles, P_4^0, $P_4^2\begin{cases}\cos(2\varphi)\\ \sin(2\varphi)\end{cases}$, $P_4^4\begin{cases}\cos(4\phi)\\ \sin(4\phi)\end{cases}$ (Stewart, 1976). Hence, the scattering factor may be written as

$$\begin{aligned}f_{hkl}=C_0\langle j_0\rangle&+\{C_{20}P_2^0(\cos\theta)\\&+C_{22}[P_2^2(\cos\theta)\cos(2\varphi)\\&+P_2^2(\cos\theta)\sin(2\varphi)]\}\langle j_2\rangle\\&+\{C_{40}P_4^0(\cos\theta)+C_{42}[P_4^2(\cos\theta)\sin(2\varphi)\\&+P_4^2(\cos\theta)\sin(2\varphi)]\\&+C_{44}[P_4^4(\cos\theta)\cos(4\varphi)\\&+P_4^4(\cos\theta)\sin(4\varphi)]\}\langle j_4\rangle,\end{aligned}$$

where θ is the Bragg angle for the reflection hkl, the parameters C_{ij} represent electron populations and $\langle j_0\rangle$, $\langle j_2\rangle$, $\langle j_4\rangle$ are the integrals $\langle j_H(K)\rangle$ $(H=0,2,4)$ defined above.

In this analysis, only reflection data from crystal II were used. The differences (SF_0-F_{core}), where F_{core} contains only the calculated contribution of the vanadium core electrons, were taken to represent the contribution of the total $3d$ charge density in the unit cell. As before, only low-angle data were used $[(\sin\theta)/\lambda<0{\cdot}6\ \text{Å}^{-1}]$. A set of structure factors was calculated using a multipole expansion of the $3d$ scattering factor, their radial part being computed by Clementi & Roetti (1974) wave functions. The set of axes $OXYZ$ were chosen as quantum axes.

Electron-population parameters were refined using a least-squares technique. Multipole functions are selectively introduced in the scattering factor expansion; the final choice was dictated by the lowest values obtained for the R factor and χ^2, defined in the usual way. The results thus obtained are

$$C_0=1{\cdot}5038\ (412),\ C_{20}=-0{\cdot}8687\ (3200),$$
$$C_{40}=0{\cdot}4466\ (7360)$$

with $R=21\%$ and $\chi^2=11$. The corresponding agreement factors for a postulated spherical model are $R=42\%$ and $\chi^2=74$.

Discussion

The values of the occupation parameters α_i obtained for crystals I and II (Table 2) clearly indicate a preferential occupation of d_{xz}- and d_{yz}-type orbitals. This corresponds to the presence, on the difference maps, of a deformation density between directions joining a pair of neighbouring ions, V^{2+} and F^-.

The main source of error in these parameters is likely to be the assumption that the asphericity of the 3*d* electrons is the only contribution to the observed difference density.

In the case of crystal II, the values of α_2 and α_3 yielding a minimum of χ^2 are negative. This can be attributed to the constraint imposed on the sum of the α_i ($i=1$ to 5): the best fit tends to occur at the highest possible values of α_4 and α_5, and this apparently forces α_2 and α_3 to be negative. Since the definition of the parameters α_i shows that negative values are meaningless, α_2 and α_3 were taken to be zero.

The results obtained from the multipole analysis show that only two multipole amplitudes, C_0 and C_{20}, are significant. C_0 is a measure of the spherical contribution of the 3*d* electrons to the scattering factor. The aspherical electron density associated with the multipole P_2^0, whose amplitude is C_{20}, shows positive lobes directed along the *Z* axis (Stewart, 1976). Hence, the negative value obtained for C_{20} evidences a deficiency of charge density along the directions $V^{2+}-F^-$. This is in agreement with the conclusion derived from the analysis based on 3*d* wave functions: the 3*d* electrons tend to avoid directions joining a pair of ions, V^{2+} and F^-.

It may be inferred from the above considerations that no significant degree of covalency could be detected in vanadium difluoride.

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Electron Density in Non-Ideal Metal Complexes. III.* Bis(hydrazine)bis(hydrazinecarboxylato)cobalt(II)

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Abstract

The difference density near the Co atom in the title compound $[Co(CH_3N_2O_2)_2(N_2H_4)_2]$ is broadly similar to that in other transition-metal complexes. The *d*-electron maxima are farther from the nucleus than the corresponding peaks for low-spin cobalt(III) complexes. The plane containing four ligand N atoms has approximate fourfold symmetry. Other sections, with ligand atoms of different types, are less symmetrical. Differences in the heights of the *d*-electron maxima are consistent with a modulating effect of interactions with second-nearest-neighbour atoms in the hydrazinecarboxylato moiety. Near the two ligand

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* Part II: Maslen, Spadaccini, Watson & White (1986).

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