Conclusion

The calculated static distortion of the S_8 molecule agrees well with the experimental observations. However the amount of distortion deduced from experiments seems to be somewhat bigger than that calculated. This observation is consistent with the preliminary comparison of the calculated and observed phonon dispersion data of Rinaldi (1973), suggesting that the potential used is somewhat too soft and the forces correspondingly too weak.

The calculation shows that the crystal forces are strong enough to cause definitely observable distortions in the molecules. The degree of distortion of S_8 is however somewhat exceptional because of the very soft E_2 internal mode which corresponds to roughly half of the distortion. Other molecules lacking such low-frequency modes would have correspondingly smaller distortions under forces of equal strength.

The energy involved in the molecular distortion, $\frac{1}{2}u\varphi u^T$, is calculated to be 0·0837 kcal/mole (5·81 × 10^{-22} joule/molecule) compared with the sublimation energy of about -25 kcal/mole (-1740×10^{-22} joule/molecule). If the intermolecular forces are constant over the small displacement u, the total crystal potential would drop by $\frac{1}{2}u\varphi u^T$ as the intermolecular potential contribution would be lowered by $u\varphi u^T$. As these forces vary slightly, the latter is reduced by a somewhat greater amount, 0·1834 kcal/mole (12·7 × 10^{-22} joule/molecule).

We anticipate little change in our main result when the accurate X-ray and neutron structural studies which are now in progress become available. Therefore the symmetrical molecule from Pawley & Rinaldi (1972), corrected for the effect of libration and A_1 distortion is probably the most accurate measure we have of octasulphur in the free state.

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Twinning in Cr-Doped VO₂

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Twinning has been studied in several samples of VO₂ containing in substitution solid solution 0·5 and 2·5 at.% Cr. The twinning is by reticular pseudo-merohedry and it is controlled by the tetragonal pseudo-symmetry of a superlattice obtained from the original monoclinic cell ($a \simeq 9\cdot1$, $b \simeq 5\cdot8$, $c \simeq 4\cdot5$ Å, $\beta \simeq 90°$) by means of the transformation $100/002/0\bar{1}0$. More than one twin law is found in every sample studied. All the theoretically possible twin laws, except one, have been observed. The possibility of twinning simulating a lattice and a space group different from the true ones has been pointed out and methods for detecting twins in these cases are given.

Introduction

In general, the structural changes occurring in metal–insulator transitions can be described in terms of small distortions of the crystal structure of one of the two phases involved in the transformation. When the distortions result in a final phase having a symmetry lower than that of the initial phase, the transition is usually associated with twin formation. The presence of twinned individuals in a sample complicates the interpretation of the diffraction patterns and, if not detected, might result in erroneous structural determinations. Therefore, a detailed analysis of twinning is always necessary in order to determine the true crystallographic parameters.

Cr-doped VO₂ undergoes a metal–insulator transi-

tion in which the high-temperature phase, with a rutile-type structure, is slightly distorted into a monoclinic structure (Marezio, McWhan, Remeika & Dernier, 1972a). As expected, single-crystal studies on this system reveal the presence of twins in the monoclinic phase. A detailed description of these twins seems to be desirable not only to characterize the crystallography of the system, but also because the same analysis can be carried out in other similar cases. In what follows we shall give the results obtained from several samples of VO_2 with 0·5 at.% Cr and VO_2 with 2·5 at.% Cr.

Theoretical predictions

The system $V_{1-x}Cr_xO_2$ ($0 \le x \le 0·025$) contains four phases very closely related. The crystal structures of these phases and their axial and structural relationships have been studied recently (Longo & Kierkegaard, 1970; Marezio, McWhan, Remeika & Dernier, 1972a, b). The crystal data obtained for the monoclinic phase M_3 of $VO_2 + 0·5$ at.% Cr and M_2 of $VO_2 + 2·5$ at.% Cr (Table 1) show that, since $\beta \simeq 90°$ and $a \simeq 2c$, the crystal lattice of Cr-doped VO_2 is consistent with a pseudo-tetragonal superlattice which can be obtained from the original cell by means of the transformation matrix $100/002/0\bar{1}0$. Under these conditions twinning controlled by the pseudo-symmetry of the superlattice has to be expected (twinning by reticular pseudo-mero-hedry) (Friedel, 1964; Donnay, 1952; Donnay & Donnay, 1959). The twin laws predicted by the theory and the corresponding twin indices and twin obliqui-

Table 1. *Crystal data* * *for* Cr-*doped* VO_2 *at room temperature*

	$VO_2 + 0·5$ at.% Cr	$VO_2 + 2·5$ at.% Cr
a	9·081 (1) Å	9·0664 (7) Å
b	5·781 (1)	5·7970 (5)
c	4·516 (1)	4·5255 (4)
β	90·91 (1)°	91·88 (1)°
Space group	$C2/m$	$C2/m$
Number of samples	1	3

* Figures in parentheses are standard deviations in the last decimal figure.
(After Marezio *et al.*, 1972a, b)

Table 2. *Possible twin laws for* Cr-*doped* VO_2

Twin axes and planes are referred to the monoclinic cells whose parameters are given in Table 1.

Twin law	Index	Obliquity	
		$VO_2 + 0·5$ at.% Cr	$VO_2 + 2·5$ at.% Cr
$[010]_{90°}$	2	*	
$(20\bar{1}) \equiv [102]_{180°}$	2	0·3°	0·1°
$(201) \equiv [10\bar{2}]_{180°}$	2	0·3	0·1
$(100) \equiv [001]_{180°}$	1	0·9	1·88
$(001) \equiv [100]_{180°}$	1	0·9	1·88

* For the twin law $[010]_{90°}$ the obliquity is not defined. The twin operation $[010]_{90°}$ relates two lattices I and II mutually oriented so that $c_{II} \wedge a_I = a_{II} \wedge \bar{c}_I = 0·9°$ for $VO_2 + 0·5$ at.% Cr and 1·88° for $VO_2 + 2·5$ at.% Cr.

ties are listed in Table 2. In the Table are also indicated the equivalent twin laws. Since the operations of the twofold axes are indistinguishable from the operations of the corresponding equivalent planes, only the planes need to be considered.

Observations

Samples of VO_2 with 2·5 and 0·5 at.% Cr were analyzed with a precession camera. Intensities were measured with an automated X-ray single-crystal diffractometer. In all cases, Mo $K\alpha$ radiation was used. Zero and upper-layer precession photographs were recorded using the unique b axis as precession axis. The diffraction patterns for layers with k even and k odd are schematically illustrated in Fig. 1(a) and (b) respectively.

Each of the samples studied was twinned on more than one law and, with the exception of $[010]_{90}$, all the twin laws were observed at least once. More specifically, the three crystals with 2·5 at.% Cr were twinned with the laws (201), (20$\bar{1}$) and (100) in all cases. In one of the samples also the twin operation (001) was observed, in addition to the previous ones. In the sample with 0·5 at.% Cr the observed twin laws were (201), (20$\bar{1}$), and (100).

The appearance of the precession diffraction patterns depends on the particular twin laws operating in each sample. Thus, the laws (100) and (001) can be easily detected as they produce doubling of the spots. On the other hand, the laws (201) and (20$\bar{1}$) are characterized by a small value of the obliquity and, therefore, the individuals twinned with these laws give reflections almost exactly superposed on each other. In fact, a spot having film coordinates hkl* is formed by the almost exact superposition of three reflections, one from each individual of the twin, having indices:

$$(hkl)_1 + \left(2l,k,\frac{h}{2}\right)_{II} + \left(2\bar{l},k,\frac{h}{2}\right)_{III}.$$

The same geometrical situation can also be described by saying that a reflection hkl has film coordinates hkl (again referred to the reciprocal axes of individual I) if it is produced by individual I, and film coordinates $2l,k,h/2$ and $2\bar{l},k,\bar{h}/2$ if it is produced by individuals II and III, respectively. Thus, spots with h and k both odd are produced only by individual I, while spots with k odd and inconsistent with the lattice parameters are produced only by individuals II and III. It follows that reflections with film coordinates hkl and $2l,k,h/2$ (or hkl and $2\bar{l},k,\bar{h}/2$), with $k = 2n + 1$, have intensities I_1 and I_2, respectively, such that

$$I_2/(I_1 + I_2) = \text{constant} . \qquad (1)$$

The intensities I_1 and I_2 and the corresponding values of the constant ratio are given in Table 3 for a number

* Film coordinates may be referred to the reciprocal axes of any one of the twinned individuals, say individual I having the most intense diffraction effects.

of reflections measured on the sample of VO$_2$ + 0·5 at.% Cr.

If twinning takes place only with the laws (201) and (20$\bar{1}$), the diffraction patterns simulate a lattice having a cell related to the true one by the axes transformation 10$\bar{2}$/010/002 and having parameters

$$a' = (a^2 + 4c^2 - 4ac \cos \beta)^{1/2}, \ b' = b, \ c' = 2c,$$

$$\cos \beta' = \frac{a \cos \beta - 2c}{2c(a^2 + 4c^2 - 4ac \cos \beta)^{1/2}}.$$

For VO$_2$ + 2·5 at.% Cr we have $a' = 13·019$, $b' = 5·797$, $c' = 9·051$ and $\beta' = 135·9°$. The diffraction patterns indexed in terms of this cell would show systematic extinctions for $h' + k' = 2n + 1$ in the class $h'k'l'$ and for $l' = 2n + 1$ in the class $h'0l'$. These extinctions simulate the space groups Cc or $C2/c$.* Twinning, how-

* General discussions on the symmetry of the complete twin and on the possibility of misinterpretation of symmetry have been given by Buerger (1954) and by Curien & Donnay (1959).

Table 3. *Reflections from individuals twinned with the laws* (201) *and* (20$\bar{1}$) *in* VO$_2$ + 0·5% Cr *sample*

Indices are given for the true cell (umprimed) and for the cell related to it by the transformation (10$\bar{2}$/010/002).

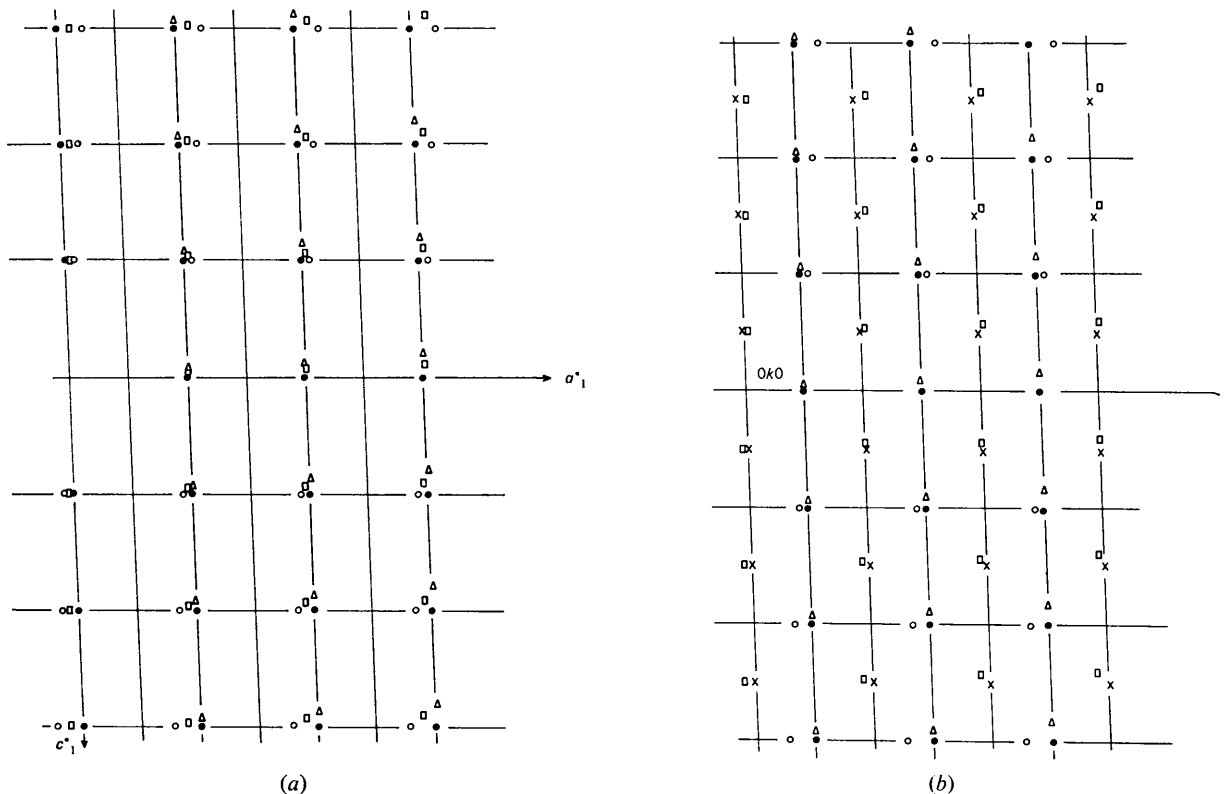| hkl $2l,k,h/2$	$h'k'l'$ $h',k',h'+l'$	I	I_2 $I_1 + I_2$	hkl $2l,k,h/2$	$h'k'l'$ $h',k',h'+l'$	I	I_2 $I_1 + I_2$
9$\bar{1}$0	9$\bar{1}$0	193	0·10	43$\frac{1}{2}$	331	25	0·11
0$\bar{1}\frac{9}{2}$	$\bar{9}$1$\bar{9}$	21		132	$\bar{3}$34	211	
1$\bar{3}$0	1$\bar{3}$0	1236	0·11	43$\frac{3}{2}$	133	44	0·13
0$\bar{3}\frac{1}{2}$	$\bar{1}$3$\bar{1}$	148		332	$\bar{1}$34	290	
1$\bar{5}$0	1$\bar{5}$0	364	0·11	67$\frac{1}{2}$	571	35	0·12
0$\bar{5}\frac{1}{2}$	$\bar{1}$5$\bar{1}$	44		173	$\bar{5}$76	261	
101$\frac{1}{2}$	911	12	0·12	83$\frac{7}{2}$	137	5	0·11
115	$\bar{9}$,1,10	87		734	$\bar{1}$38	42	
81$\frac{1}{2}$	711	60	0·13	63$\frac{5}{2}$	135	17	0·11
114	$\bar{7}$18	414		533	$\bar{1}$36	132	

(a)   (b)

Fig. 1. Appearance of precession diffraction patterns for layers with (a) k even and (b) k odd. The black dots represent the reciprocal nodes of the individual with the strongest reflections (individual I). The open circlets and the triangles represent the nodes repeated by the twinning planes (100) and (001), respectively. The crosses represent the nodes repeated by the planes (201) and (20$\bar{1}$) and the squares the nodes repeated by the operation [010]$_{90°}$.

ever, can be detected in two ways. First, the reflections $h'k'l'$ with $k'=2n$ are present only if $l'=2n$. This condition is not required by any space group and indicates the presence of twins. Secondly, the ratio of the intensities of reflections $h'k'l'$ and $\bar{h}',k',h'+l'$ (or $h'k'l'$ and $h',k',-h'-l'$) is constant (see Table 3). This result indicates that the sample is formed by at least two distinct individuals rather than being a single crystal.

By increasing the chromium content in VO_2, the values of a and $2c$ become closer and the obliquity associated with the laws (201) and (20$\bar{1}$) decreases. It is therefore reasonable to expect that these laws become more frequent with increasing amount of chromium in the sample. The results obtained in the present study seem to confirm this deduction. In fact, while the value of ratio (1) indicates that in $VO_2+0.5$ at.% Cr only 11 % of the total volume of the sample belongs to the individuals twinned with laws (201) and (20$\bar{1}$), in $VO_2+2.5$ at.% Cr about 40% of the total volume belongs to these individuals. Twins in which only the laws (201) and (20$\bar{1}$) are operative are, therefore, more probable in samples of VO_2 with a high chromium content. In these cases, unless twinning is detected, the systematic extinctions will inevitably lead to erroneous space groups.

Note added in proof: N.m.r. measurements, obtained while this paper was in press, seem to indicate that the

symmetry of the M_3 phase is lower than $2/m$ (H. Launois & T. M. Rice, private communication). For the sample of $VO_2+0.5$ at % Cr, therefore, the operation (010) (or [010]$_{180°}$) may become a possible twin operation with vanishingly small obliquity (twinning by high-order merohedry, Friedel, 1964). This twinning, if present, cannot be detected by X-ray measurements at room temperature and it has no bearing on the interpretation of the other twins. All the conclusions obtained in the paper remain, therefore, unchanged.

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Dyadics and the Variances and Covariances of Molecular Parameters, Including those of Best Planes*

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Expressions are derived for the variances and covariances of molecular parameters by combining the error propagation equation and the formalism of Gibbs' dyadics. The resulting formulas concern bond angles, bond vectors and distances, torsion angles, the parameters that describe the best plane fitted to a set of atoms, and the dihedral angle between two such planes. All results include covariance terms between the coordinates of different atoms, an important example being the torsion angle defined by atoms related by a twofold axis. An Appendix concerns the transformation properties of covariance matrix elements.

In this paper a general method is developed for obtaining the variances and covariances of molecular parameters, such as bond and torsion angles, from the positional covariance matrices of the atoms defining these parameters. Substantial use is made of the del operator, vectors, and dyadics (*e.g.*, Gibbs & Wilson, 1929; Wills, 1931; Zachariasen, 1944; Patterson,

1959). Dyadics are relatively unfamiliar, and matrices or tensors might have been employed instead. However, the use of dyadics places the cross product at our disposal, which will prove fruitful. Instead of the customary covariance matrix of the atomic coordinates we shall introduce a covariance dyadic, a procedure that is justified in an Appendix. In turn, some of our results are in the form of covariance dyadics rather than of covariance matrices. We shall first investigate

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* Contribution No. 4287.