

(see § 1) and show that one finds 24 subgroups, each one occurring twice.

Remark on tabulation

Table 6 shows what the tabulation of the symmetry block, general positions and subgroups look like for $I_{ban}^{ccm} = I_{ban} - D_{2h}^{26}$. The author has tabulated in a similar way all the C groups (D_{2h}^{17} to D_{2h}^{22}) and I groups (D_{2h}^{25} to D_{2h}^{28}).*

* These tables are available as photocopies which may be purchased from the author or obtained from the deposit with the British Library Lending Division (Supplementary Publication No. SUP 31500: 14 pp., 1 microfiche) through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

In the tables deposited under the IUCr auxiliary publication scheme, the reader will also find the corresponding tables for the two F groups $Fmmm - D_{2h}^{23}$ and $Fddd - D_{2h}^{24}$ with self-explanatory notations.

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Determination by X-ray Diffraction of Interstitial Concentrations of Vanadium Ions in Disordered VO_x

BY M. MORINAGA AND J. B. COHEN

Department of Materials Science and Engineering, The Technological Institute, Northwestern University, Evanston, Illinois 60201, U.S.A.

(Received 9 October 1975; accepted 2 December 1975)

Integrated intensities were measured from VO_x single crystals with $x = 0.80, 0.94, 1.01, 1.11$ and 1.25 . A least-squares refinement was carried out for the scale factor and the isotropic temperature factors of vanadium and oxygen ions for each composition, for a range of interstitial vanadium contents. The R values after the refinement were 0.04–0.05. There are vanadium ions at tetrahedral interstitial sites, the concentration of which changes from 0–0.5% to 3% with composition x ; this confirms quantitatively previous studies which employed dynamical electron diffraction effects. The temperature factors of vanadium (B_v) and oxygen (B_o) increase with x ; $B_v = 1.02\text{--}1.38 \text{ \AA}^2$ and $B_o = 0.58\text{--}1.24 \text{ \AA}^2$. The composition dependence of the overall temperature factor is similar to that of the lattice parameter. The 002 structure factor for electrons U_{002} and the critical voltage E_c at which the second-order Kikuchi line disappears were calculated for VO_{0.82} and VO_{1.20}, using the individual temperature factors determined by this study. The 002 structure factors measured by the critical-voltage and the intersecting-Kikuchi-line method [Watanabe, Andersson, Gjønnes & Terasaki (1974). *Acta Cryst.* A30, 772–776] were in agreement within less than 2%. The results support the idea that the ionic state of the cation lies between neutral and singly ionized.

Introduction

Vanadium monoxide is stable over a wide range of compositions at high temperature from VO_{0.8} to VO_{1.3} (Schönberg, 1954; Andersson, 1954; Westman & Nordmark, 1960; Stenström & Westman, 1968). Its structure is that of NaCl with a large number of vacancies on both vanadium and oxygen sublattices. The concentration of vanadium and oxygen vacancies changes with composition (Banus & Reed, 1970; Banus, Reed & Strauss, 1972). Even at stoichiometry about 15% of both sublattices are vacant. The existence of interstitial (tetrahedral) vanadium ions for oxygen-rich compositions has been reported (Høier & Andersson, 1974). Thus the defect structure is quite

complicated. The observed diffuse scattering exhibits a composition dependence (Andersson & Gjønnes, 1970; Andersson & Taftø, 1970; Bell & Lewis, 1971; Hayakawa, Morinaga & Cohen, 1973; Andersson, Gjønnes & Taftø, 1974) which appears to be related to the Fermi surface of VO_x (Hayakawa *et al.*, 1973). At high temperatures it has been suggested that in VO_{1.23} there are vacancy clusters each involving one interstitial vanadium surrounded by four vanadium vacancies (Andersson *et al.*, 1974). Quantitative comparisons of scattering of such defects to measured data have not yet been made. It is interesting to note that this proposed defect structure is quite similar to that for wüstite, Fe_xO (Koch & Cohen, 1969; Cheetham, Fender & Taylor, 1971). An ordered structure near VO_{1.2–1.3} has been

observed below about 800°C (Magnéli, Andersson, Åsbrink, Westman & Holmberg, 1958; Westman, 1960; Bell & Lewis, 1971; Andersson & Gjønnes, 1970). Recent electron diffraction studies (Høier & Andersson, 1974; Watanabe, Andersson, Gjønnes & Terasaki, 1974) support a structure involving ordered arrangements of such vacancy clusters but the details of the arrangement still remain to be determined.

Recently Watanabe *et al.* (1974) have determined the interstitial concentrations of vanadium ions and the overall temperature factors for VO_{0.82} and VO_{1.20} by combining the critical-voltage and intersecting-Kikuchi-line methods, which are dynamical effects in electron diffraction. The atomic scattering factors of pure metals determined by the critical-voltage method agrees well (better than 2%) with theoretical and experimental values (determined by X-rays) (Watanabe, Uyeda & Fukuhara, 1969; Arii, Uyeda, Terasaki & Watanabe, 1973; Fujimoto, Terasaki & Watanabe, 1972). However, the result depends on the temperature factor and therefore this method is limited to materials for which this factor is well known. Since the low-index structure factor determined by the intersecting-Kikuchi-line method is insensitive to the temperature factor, the combination of these methods may be useful even if there are attendant losses in accuracy. However, in the study of oxides whose ionic state is unknown and for which the component ions may have individual temperature factors, the problem cannot be solved explicitly even by the combined use of these methods. It was necessary with VO_x to assume the ionicity and use an overall temperature factor, and the resultant uncertainties concerning tetrahedral composition are not clear.

In this paper, integrated X-ray intensities from single crystals of VO_x are reported. By means of a least-squares analysis the interstitial concentration of vanadium, the isotropic temperature factors of vanadium and oxygen and also the overall temperature factor were determined over the range of existence of VO_x. Comparisons with the electron diffraction methods provide proof of the validity and limits of application of each of the methods.

Experimental

(a) Specimen preparation

Polycrystalline specimens of VO_x were prepared by single-arc and tri-arc melting (Reed, 1967; Reed & Pollard, 1968) from appropriate mixtures of V₂O₅ and high-purity vanadium under an argon atmosphere. A large single crystal of VO_{1.25} was grown by the arc-Czochralski technique (Reed, 1967, 1969; Reed & Pollard, 1968). Suitable single crystals ~2 mm in diameter of other compositions were prepared from large grains obtained by heating specimens at 1450°C or 1700°C under an argon atmosphere, purified by passing the gas over heated titanium sponge.

Compositions were determined by measuring the

weight change of a sample (weighing approximately 0.4 g) after combustion in air to V₂O₅ for five days at about 675°C (Banus & Reed, 1970; Reuther & Brauer, 1971; Watanabe *et al.*, 1974). Once the combustion was complete, the weight did not change during subsequent heating for two to three days within the error of measurements (± 0.1 mg); this error yields an uncertainty of at most 0.002 in x . Banus *et al.* (1972) estimate the total error in x with this method to be 0.008–0.01. Employing the data of Banus *et al.* (1972) this uncertainty yields errors of $\pm 0.2\%$ and $\pm 0.6\%$ in estimates of vacancy concentrations of vanadium and oxygen respectively.

Composition *vs* lattice parameter differs slightly in available publications (Westman & Nordmark, 1960; Stenström & Westman, 1968; Takeuchi & Suzuki, 1967; Banus & Reed, 1970; Banus *et al.*, 1972; Reuther & Brauer, 1971; Watanabe *et al.*, 1974). From powder patterns taken in this study, the lattice parameter *vs* x (Fig. 5) is very similar to that reported by Banus *et al.* (1972).

The VO_{1.25} specimen was quenched from 1050° into ice water. The other specimens were slowly cooled from 1450°C. The X-ray powder patterns showed only the disordered phase of VO_x.

Single crystals were ground to a nearly spherical shape of about 0.3 mm in diameter in a Bond (1951) grinding device. Integrated intensities were measured only with crystals showing small unbroken Laue spots.

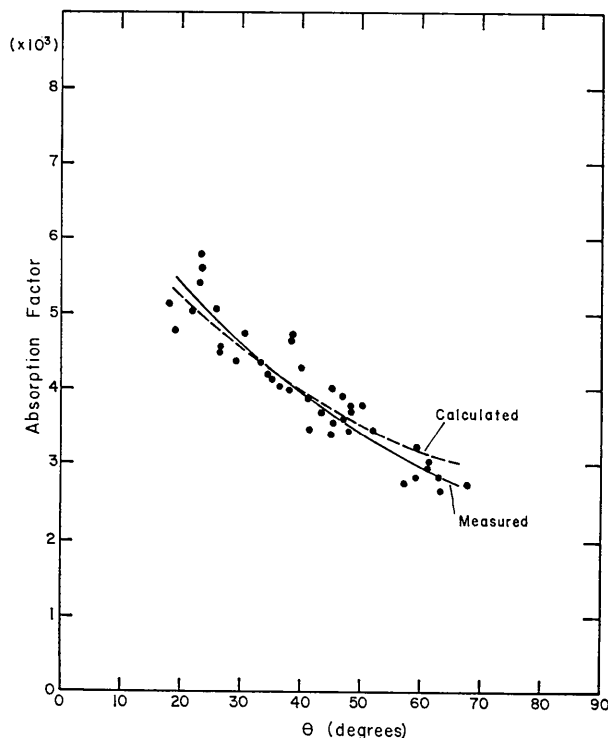


Fig. 1. Change of absorption factor with angle. Measured values (points) correspond to the counting times (s) of fluorescent intensity necessary for 2000 counts.

(b) X-ray measurements

Intensity data were collected with a General Electric diffractometer equipped with a quarter-circle goniostat, a scintillation detector, pulse-height discrimination

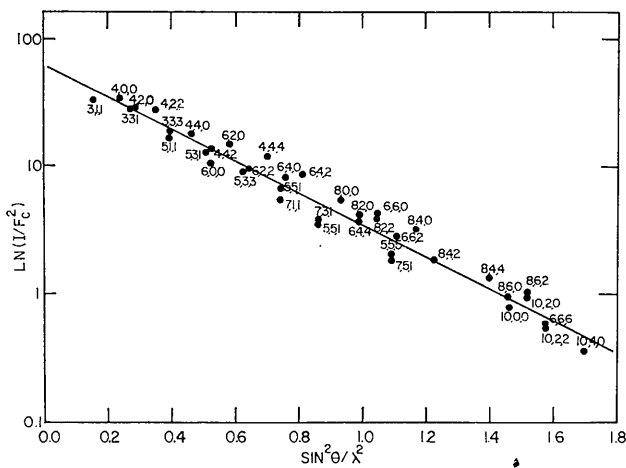


Fig. 2. $\ln(I/F_c^2)$ vs $(\sin^2 \theta/\lambda^2)$ for $\text{VO}_{1.25}$.

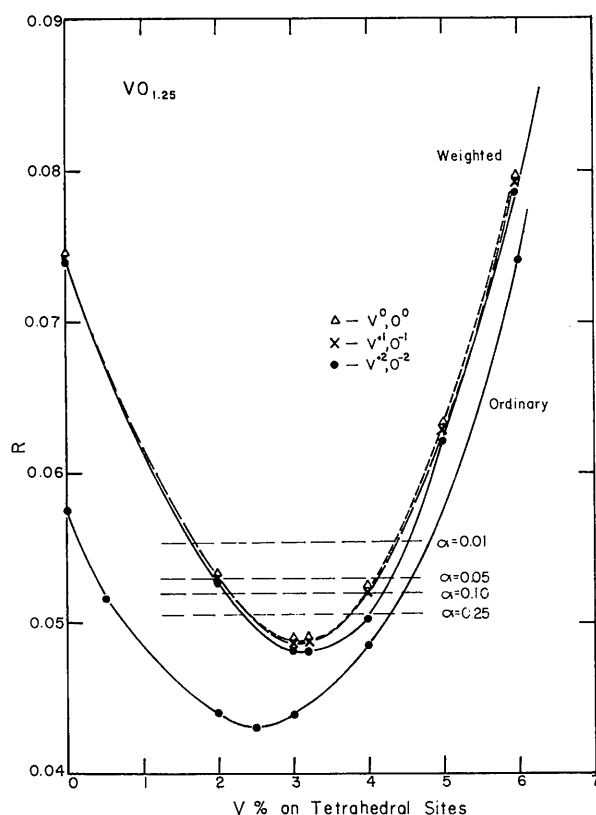


Fig. 3. Change of R values with interstitial concentration of vanadium ions in $\text{VO}_{1.25}$. Ordinary $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$. Weighted $R = (\frac{\sum W_i (|F_o| - |F_c|)^2}{\sum W_i |F_o|^2})^{1/2}$. The weighting scheme was that suggested by Corfield, Doedens & Ibers (1967). The weighted R was calculated for three ionic states.

and controlled by a mini-computer (Richesson, Morrison, Cohen & Paavola, 1971). Filtered $\text{Mo } K\alpha$ radiation was employed. Integrated intensities were measured by the normal θ - 2θ step-scan technique in increments of 0.01° in 2θ . The step-scan was repeated automatically until the statistical accuracy of the net intensity above background was less than 2%. Since the dead time of the counting circuits including the mini-computer was large ($23.8 \mu\text{s}$), the intensity was reduced to less than 1000 c.p.s. (except for a few low-angle peaks) with a Zr filter and by adjusting the operating condition of the X-ray tube. Some 35–40 peaks were measured for each composition, most of which were between 40° and 140° in 2θ . Several strong peaks at lower angles were not measured because of uncertainties in corrections due to dead time and extinction effects.

The measured integrated intensities were corrected for the Lorentz-polarization factor and absorption. This absorption correction was obtained by measuring the intensity of fluorescent radiation at each crystal orientation used to obtain diffraction peaks (Koch & Cohen, 1969), adjusting the pulse-height analyzer to accept $V K\alpha$ radiation but reject the $\text{Mo } K\alpha$ radiation. The angular dependence of this fluorescent intensity is shown in Fig. 1. The intensities did not vary smoothly with angle because of deviations in sphericity of the crystals. For comparison, the calculated absorption factor corresponding to $\mu R = 1.8$ is given by a dotted line where μ is the linear absorption coefficient and R is the radius of a spherical specimen. The average of the measured fluorescent intensities (full line) shows a slightly larger angular dependence than the calculated one due to the difference of absorption coefficients of the fluorescent $V K\alpha$ and incident $\text{Mo } K\alpha$ radiations. This leads to a discrepancy of at most 8–10% in the correction. The contribution of temperature diffuse scattering to the measured intensities was not subtracted since there are no available data on the elastic constants of VO_x .

Results and discussion

Plots of $\ln(I/F_c^2)$ vs $(\sin^2 \theta/\lambda^2)$ for $\text{VO}_{1.25}$ are shown in Fig. 2, where I is measured intensity after corrections, F_c the calculated structure factor ignoring tetrahedral ions and λ is the wavelength of X-rays. The concentrations of vanadium and oxygen vacancies were taken from the results of Banus *et al.* (1972). The overall temperature factor was 1.43 \AA^2 . The linearity in this figure can be improved if vanadium ions are introduced on tetrahedral sites. This was included in a least-squares refinement employing the *ORFLS* computer program (Busing, Martin & Levy, 1960), as modified by Ibers. The ordinary and weighted R values were calculated and the refinement was on the scale factor and isotropic temperature factors of vanadium and oxygen ions for a series of specific tetrahedral contents. [The concentrations of vanadium vacancies were

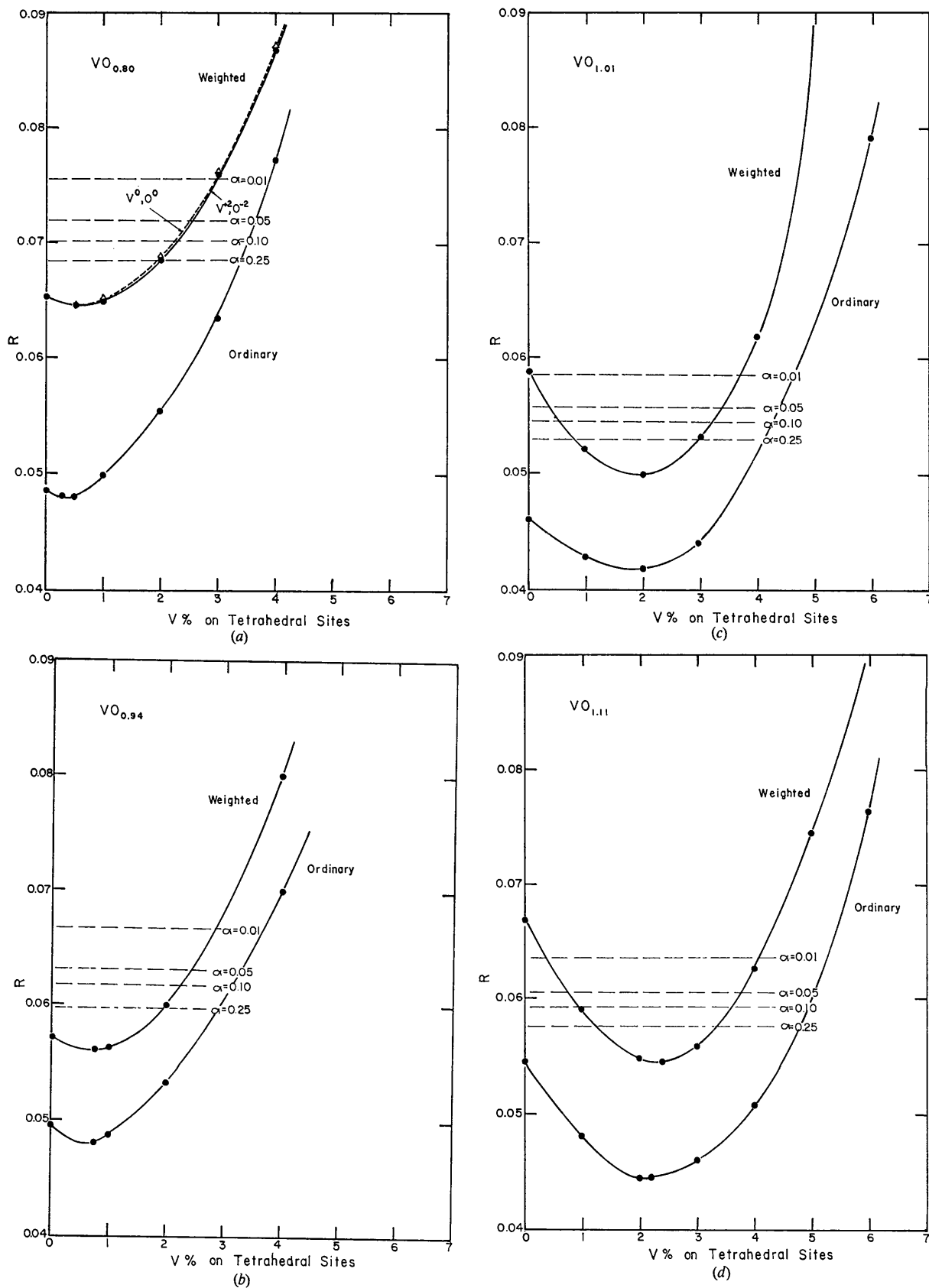


Fig. 4. Change of R values with interstitial vanadium content in (a) VO_{0.80}, (b) VO_{0.94}, (c) VO_{1.01} and (d) VO_{1.11}.

adjusted as the reported values (Banus *et al.*, 1972) do not include the tetrahedral occupation.] The results for $\text{VO}_{1.25}$ are shown in Fig. 3. The minima in the R values were found at about 2.5% (ordinary R) and 3.1% (weighted R) for the tetrahedral occupation factor, *i.e.*, the probability of finding vanadium ions in the tetrahedral sites. These calculations were done for three ionic states (V^0, O^0), ($\text{V}^{+1}, \text{O}^{-1}$) and ($\text{V}^{+2}, \text{O}^{-2}$) using the corresponding atomic scattering factors. An anomalous-dispersion correction for Mo $K\alpha$ radiation was taken into account for vanadium (*International Tables for X-ray Crystallography*, 1962) but not for oxygen. The ionic state did not have any appreciable effect on the R value as might be expected, since the measured data were taken at relatively high angles where the scattering factors are insensitive to the configuration of the outer electrons. The temperature factors of vanadium and oxygen ions are $B_V = 1.37 \pm 0.037 \text{ \AA}^2$ and $B_O = 1.26 \pm 0.052 \text{ \AA}^2$ respectively. When the temperature factors of vanadium ions at octahedral and tetrahedral (interstitial) sites were treated separately in a refinement, the weighted R values showed a minimum at 2.8%. In this case the temperature factors were $B_{V(\text{octa})} = 1.39 \pm 0.037 \text{ \AA}^2$, $B_{V(\text{tetra})} =$

$1.28 \pm 0.187 \text{ \AA}^2$ and $B_O = 1.21 \pm 0.050 \text{ \AA}^2$. Thus, the minimum position is $(2.8 \pm 0.3)\%$ for $\text{VO}_{1.25}$. The significance test discussed by Hamilton (1965) was applied to the weighted R -value curves. In Fig. 3 the values of $\alpha = 0.25, 0.10, 0.05$ and 0.01 are shown, corresponding to the levels of 75, 90, 95 and 99% confidence limits respectively. If the 95% confidence level is chosen, the tetrahedral concentration is $3.1 \pm 1.2\%$.

The use of absorption factors estimated by μR gave a slightly smaller R value, but the minimum point in the R -value curve did not change significantly. Similar analyses were carried out for $x = 0.80, 0.94, 1.01$ and 1.11 . The results are shown in Fig. 4(a-d). The concentrations of interstitial vanadium ions changes with composition. The vacancy concentrations of vanadium and oxygen ions determined with published values for the density, lattice parameter and composition (x) may not be highly accurate. But a refinement of these vacancy concentrations along with the other variables revealed that the present results for interstitial concentrations was most likely even allowing for a small change in vacancy concentration.

The existence of tetrahedral vanadium ions for VO_x at $x < 1$ is not clear because of the shallow minimum in the R value curves (Fig. 4). However, the plots of overall temperature factors and lattice parameter in Fig. 5 suggests that there is indeed tetrahedral occupation even for $x < 1$.

The overall temperature factor (1.43 \AA^2) obtained from the slope of $\ln(I/F_0^2)$ vs $(\sin^2 \theta/\lambda^2)$ is very large compared to other transition-metal monoxides [*e.g.* $\text{Fe}_{0.9}\text{O}$: 0.79 \AA^2 (Koch & Cohen, 1969), TiO_x : $0.56\text{--}0.80 \text{ \AA}^2$ (from Watanabe & Terasaki, 1972)], indicating that there are large static and thermal displacements of ions in VO_x which increase with composition x . The interstitial vanadium ions as well as the large number of vacancies may contribute to this large temperature factor.

It is well known that lattice parameter is one of the important quantities to consider in this type of oxide as it is related to the bonding of ion pairs and to the physical properties of these oxides. For instance, in VO_x Goodenough (1972) suggests that the change of electron conductivity with composition x can be attributed to the change of cation-cation separation. The electron hopping model which is proposed as the dominant conduction mechanism for $x < 1$ is related to local lattice distortion through electron-lattice interactions. Thus, in VO_x the overall temperature factor also appears to be an important parameter.

Comparisons with the critical-voltage and the intersecting-Kikuchi-line methods

There are several methods for determining the structure factors from dynamical effects in electron diffraction [see reviews by Cowley (1969) and Uyeda (1974)]. Among these, the critical-voltage and intersecting-Kikuchi-line methods are interesting because, as men-

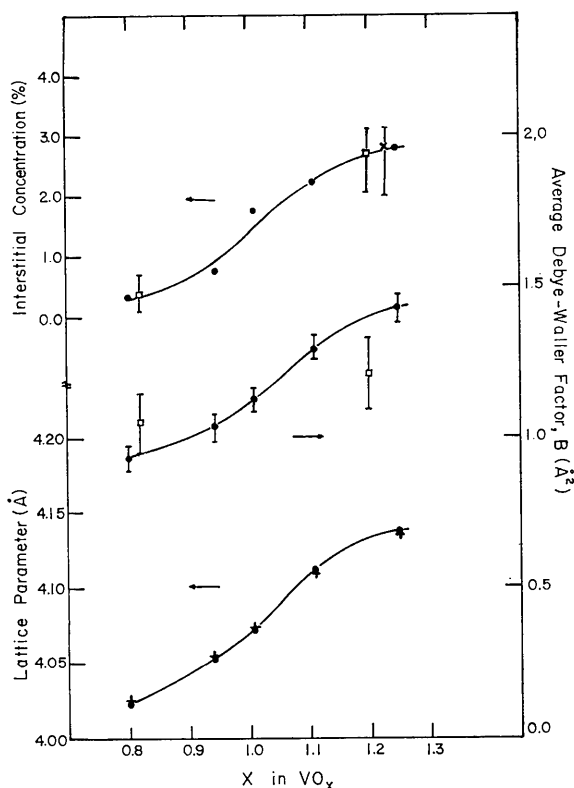


Fig. 5. Composition dependence of the interstitial concentration of vanadium ions, the overall temperature factor and the lattice parameter. ● Present results - X-rays, □ Watanabe *et al.* (1974) - critical-voltage and intersecting-Kikuchi-line methods, × Høier & Andersson (1974) - intersecting Kikuchi-line method, + Banus *et al.* (1972).

tioned above, they are purported to be of high accuracy and are simple experimentally.

Watanabe, Uyeda & Kogiso (1968) observed the disappearance of second-order Kikuchi lines at a certain accelerating voltage E_c with a row of spots operating ('systematic reflections'). This is the so-called critical-voltage method (Lally, Humphreys, Metherell & Fisher, 1972) and is currently interpreted as due to the relativistic change of electron mass with accelerating voltage which influences the effective structure factors. Many-beam dynamical calculations show a zero or minimum intensity of a second-order reflexion. The observed critical voltage for VO_{0.82} and VO_{1.20} are 312 ± 5 kV and 430 ± 9 kV respectively (Watanabe *et al.*, 1974), from the disappearance of 004 Kikuchi lines.

Gjønnnes & Høier (1971) proposed the intersecting-Kikuchi-line method which can be interpreted essentially by three-beam dynamical theory (Kambe, 1957). The splitting near intersecting Kikuchi lines is proportional to the Fourier coefficients of the crystal potential and hence to the structure factor. The contrast of a Kikuchi line is assumed to be proportional to the width of the corresponding gap in the dispersion surface. The observed structure factors U_{002} of VO_{0.82} and VO_{1.20} are $(6.3 \pm 0.1) \times 10^{-2} \text{ \AA}^{-2}$ and $(5.6 \pm 0.1) \times 10^{-2} \text{ \AA}^{-2}$ respectively (Watanabe *et al.*, 1974).

Watanabe *et al.* (1974) have determined the interstitial concentration of vanadium ions and the overall temperature factors by the combined use of these experiments. Their results are given in Fig. 5. The agreement with X-ray results is good and consequently the combination of these electron diffraction methods can indeed be useful.* But care is needed when the component ions have different temperature factors. As shown in Fig. 6, this difference increases in VO_x with decreasing x . Using the temperature factors in Fig. 6, the 002 structure factor for electrons U_{002} and the critical voltage E_c were calculated. [The other values employed in the calculation were the same as in Watanabe *et al.* (1974).] The critical voltage was calculated assuming the second B e approximation (Uyeda, 1968), since Watanabe *et al.* (1968), Watanabe & Terasaki (1971), Arii *et al.* (1973) and Fujimoto *et al.* (1972) have shown that this calculation agrees almost exactly with the many-beam calculation developed by Fukuhara (1966). The results are given in Fig. 7 for VO_{0.82} and in Fig. 8 for VO_{1.25}. The dashed bands in the figure indicate the observed values with their associated errors. It is apparent that U_{002} and E_c are quite sensitive to the ionic state. The difference in structure factor between the critical-voltage and intersecting-Kikuchi-line methods is about 1.7% for VO_{0.82} and 0.8% for VO_{1.20} regardless of the ionicity. This is very good agreement in spite of the uncertainty in the

measurement of the line separation near Kikuchi bands.

With respect to the ionic states in VO_x, for instance in VO_{0.82}, the difference in structure factor is only about 2.4% between (V⁰, O⁰) and (V⁺¹, O⁻¹) and 1.1% between (V⁺¹, O⁻¹) and (V⁺², O⁻²). These values are comparable to the error in electron diffraction methods. But the comparison of the present calculation with the most probable X-ray results (indicated by arrows in Figs. 7 and 8) suggests that the ionic state in VO_x is either neutral or between neutral and singly-ionized. It is likely that the atoms in VO_{0.82} are neutral (Watanabe *et al.*, 1974) because of the large difference of critical voltage between (V⁰, O⁰) and (V⁺¹, O⁻¹) in Fig. 7(a). The trend to ionization may increase with composition x (compare Figs. 7 and 8). Most of the band calculations reported for VO have been carried out assuming neutral or singly ionized states (*e.g.*, Norwood & Fry, 1970; Tewari, 1972). Recent calculations by the molecular-orbital method (Gubanoc, Kasimov & Kuremaev, 1975) suggest that the charge on the vanadium ion is +0.66.

The 1~2% discrepancy in structure factors obtained by both electron diffraction methods leads to a difference of $\pm 0.2 \sim 0.3 \text{ \AA}^2$ in overall temperature factor. This is so large because of the low scattering angle in these methods. This results in large changes in the critical voltage E_c . Thus, the combined methods should be carefully applied, especially in a case where there are large differences in the temperature factors of the component ions.

A similar study in TiO_x would be interesting since there is an inconsistency in the ionic state estimated

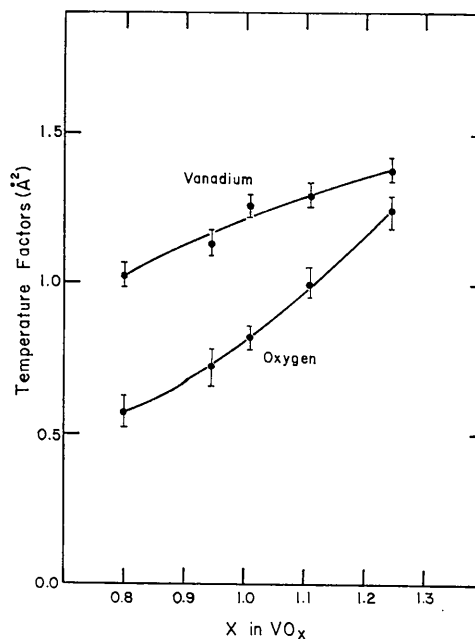


Fig. 6. Change of temperature factors of vanadium and oxygen ions with composition x .

* There is good agreement with the results of Høier & Andersson (1974) also and they employed only one method. However, they assumed a certain ionicity.

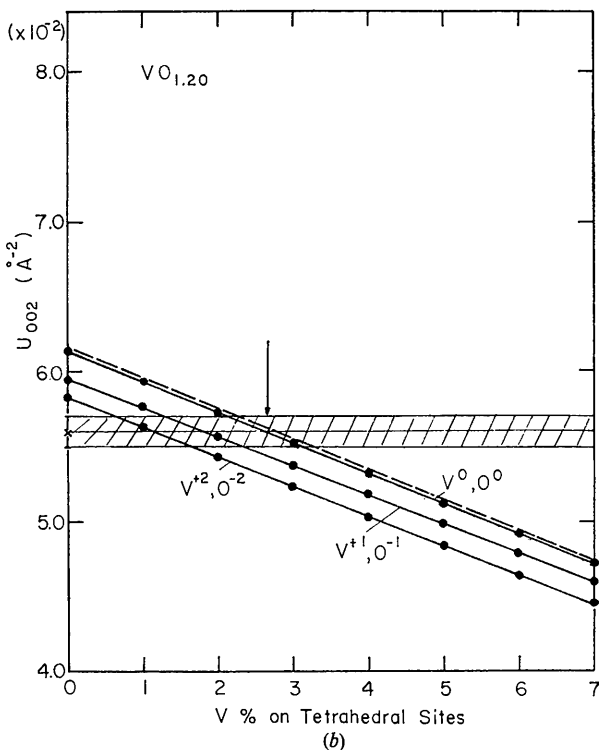
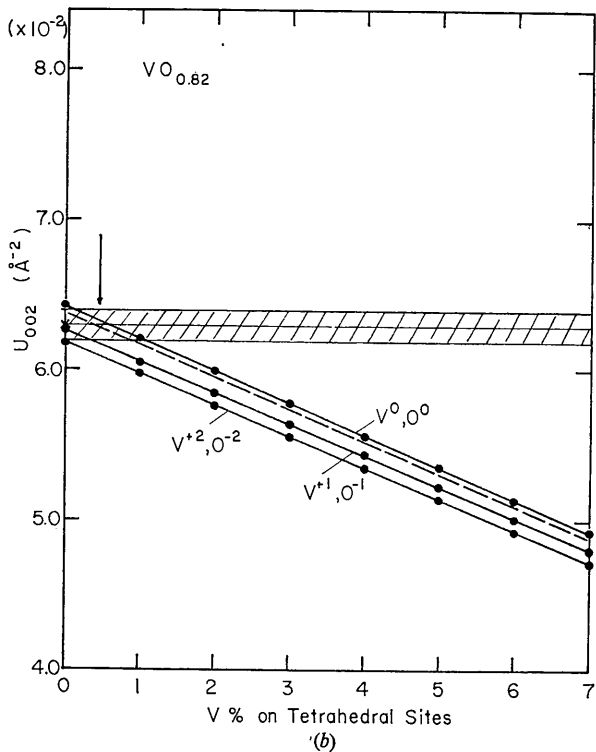
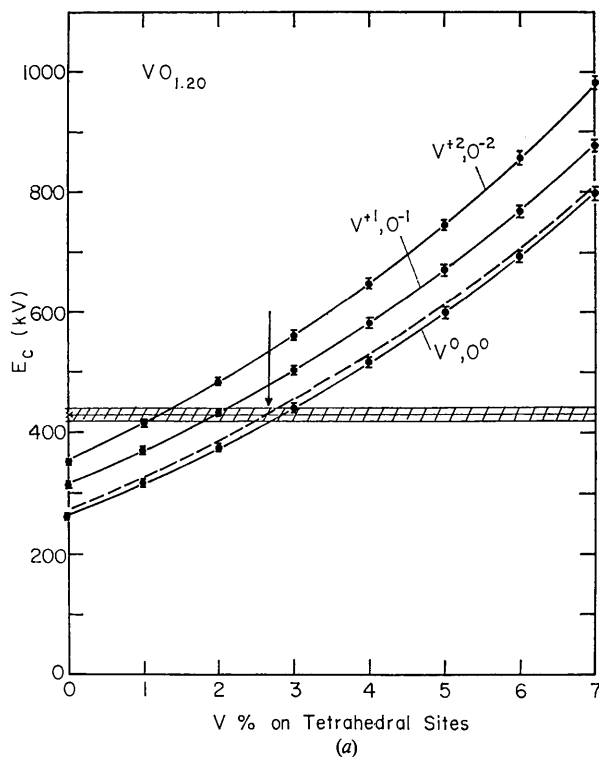
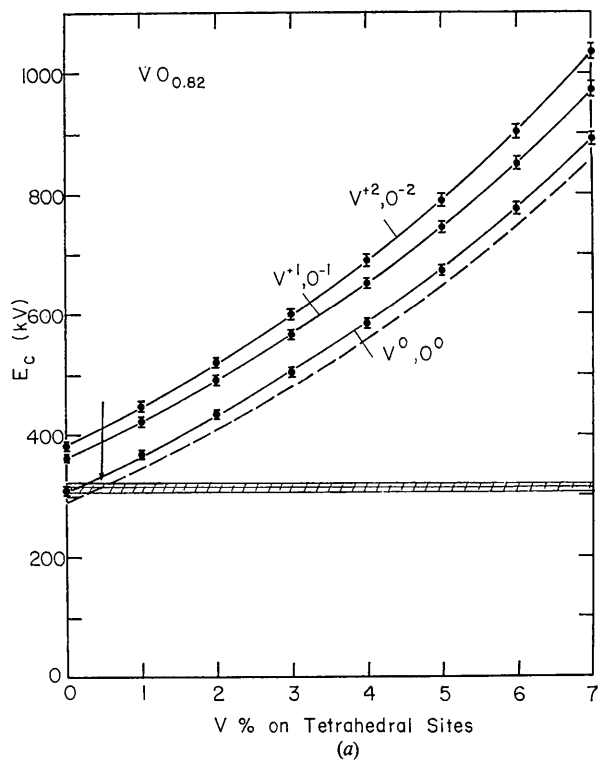


Fig. 7. (a) Critical voltage E_c vs. tetrahedral content for three ionic states of $\text{VO}_{0.82}$. Atomic scattering factors V^0, O^0 ; Doyle & Turner (1968), V^{+1}, O^{-1} ; V^{+1} : Watson & Freeman (1961); O^{-1} : Cromer & Mann (1968) and V^{+2}, O^{-2} ; V^{+2} : Doyle & Turner (1968); O^{-2} : Tokonami (1965). (b) The 002 structure factor U_{002} vs. tetrahedral content for three ionic states of $\text{VO}_{0.82}$. The dashed line is for the overall temperature factor $B = 1.05 \text{ \AA}^2$ (Watanabe *et al.*, 1974).

Fig. 8. (a) Critical voltage E_c vs tetrahedral content for three ionic states of $\text{VO}_{1.20}$. (b) The 002 structure factor U_{002} vs tetrahedral content for three ionic states of $\text{VO}_{1.20}$. The dashed line is for the overall temperature factor $B = 1.21 \text{ \AA}^2$ (Watanabe *et al.*, 1974).

from the Compton profile and from structure-factor measurements (Terasaki, Watanabe, Fukamachi, Ho-soya & Shimizu, 1972).

Conclusions

The results obtained in the present experiment are summarized in Table 1. It is noted that there are interstitial metal ions in VO_x just as in Fe_xO (Koch & Cohen, 1969; Cheetham, Fender & Taylor, 1971) and CoO–NiO solutions (Stiglich, Whitmore & Cohen, 1973). The large overall temperature factor indicates that there are large static and thermal displacements of ions in VO_x. The results support the idea that the ionization of vanadium in VO_x is between that for neutral and singly ionized states.

The critical-voltage and the intersecting-Kikuchi-line methods have been shown to be useful for the quantitative determination of low-order structure factors of oxides. In VO_x the two methods agree within an error of less than 2%. This small discrepancy may be due to errors in measuring the separation of Kikuchi lines.

Compared to these electron diffraction methods, the X-ray method is not nearly as quick for determining interstitial contents. The preparation of single crystals is inevitably required to get a high accuracy. However, the X-ray method is useful in the sense that many unknown factors can be determined by a least-squares refinement of measured intensities, whereas the analyses of electron diffraction effects become difficult. For example, the individual temperature factors determined by X-rays are required to determine ionicity with the electron diffraction methods.

The authors thank Dr T. B. Reed and Mr R. Fahey at Lincoln Laboratories–M.I.T. for the opportunity to use their tri-arc furnace for growing VO_x single crystals and Dr J. A. Ibers for useful advice during least-squares analyses. This work was supported by the U.S. Air Force of Scientific Research, Office of Aerospace Research, Grant No. AF-AFOSR-73-2431.

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Table 1. *Defect structure of VO_x*

The errors were established in the following way. The uncertainty in x is ± 0.01 as indicated in the text. This leads to an uncertainty in the percentage of oxygen vacancies of ± 0.6 and in the percentage of vanadium vacancies of ± 0.2 , and hence, to the uncertainty given in the table in % of V interstitials of ± 0.4 . The refinements discussed in the text were carried out at fixed composition, fixed percentage of oxygen vacancies and fixed total percentage of V vacancies plus tetrahedral vanadium – at each concentration of tetrahedral vanadium. Subsequently, a refinement was made of V and O vacancy concentration, the scale factor and temperature factors for each tetrahedral concentration. The resultant concentration range of V vacancies for 90% confidence limits on the tetrahedral composition from the first set of refinements was outside the range set by the uncertainty in composition, x . Accordingly, half this range was taken as the error for vanadium vacancy concentration.

Composition x	0.80	0.94	1.01	1.11	1.25
Percentage of vanadium vacancies on octahedral sites	11.8 ± 1.0	15.2 ± 1.4	18.1 ± 1.4	21.3 ± 1.6	26.2 ± 1.4
Percentage of vanadium on tetrahedral sites	0.4 ± 0.4	0.8 ± 0.6	1.5 ± 0.6	2.2 ± 0.7	2.8 ± 0.6
Percentage of oxygen vacancies	28.5 ± 0.6	18.6 ± 0.6	14.1 ± 0.6	7.5 ± 0.6	1.1 ± 0.6
Number of interstitials per unit of the ordered structure V ₅₂ O ₆₄ (Andersson & Gjønnes, 1970)	0.5 ± 0.5	1.0 ± 0.8	1.9 ± 0.8	2.8 ± 0.9	3.6 ± 0.8

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The Debye–Waller Factor of Nickel Measured at High Scattering Vectors by Pulsed Neutron Powder Diffraction

BY C. G. WINDSOR AND R. N. SINCLAIR

Materials Physics Division, AERE, Harwell, Oxon OX11 0RA, England

(Received 12 September 1975; accepted 16 December 1975)

The Debye–Waller factor of nickel has been measured by powder neutron diffraction over the range of scattering vectors Q from 10 to 24 \AA^{-1} ($\sin \theta/\lambda$ from 0.8 to 2.0 \AA^{-1}). Pulses of epithermal neutrons produced by the Harwell LINAC were scattered from a flat sample at nearly back-scattering angles ($2\theta = 150^\circ$), and observed as a function of their wavelength determined from their time of flight over a 4.6 m flight path. The resolution in d spacing was observed to be nearly constant at about $\Delta d/d = 1\%$ over the above Q range. After background subtraction, calibration using a standard vanadium scatterer, and corrections for absorption, the powder pattern was analysed using the techniques of profile analysis, in which a computed powder profile is least-squares fitted directly to the observed profile. The profile refined to an χ^2 factor of 17%, giving a simple Debye–Waller factor $\exp(-2B \sin^2 \theta/\lambda^2)$ with $B = 0.34 \pm 0.04 \text{\AA}^2$. This value is appreciably less than the values of order 0.42 \AA^2 obtained by neutron measurements at low Q . The inclusion of the fourth-order term $\exp(-2C \sin^4 \theta/\lambda^4)$ predicted by anharmonic theory raised the fitted harmonic coefficient to $B = 0.37 \pm 0.04 \text{\AA}^2$ in good agreement with X-ray and theoretical values, with $C = -0.012 \pm 0.006 \text{\AA}^4$.

Introduction

The accurate determination of thermal and other parameters in crystallography depends to a considerable extent on the extension of Bragg intensity measurements to high values of the scattering vector $Q = 4\pi \sin \theta/\lambda$. This arises because the spatial resolution obtained from a structure refinement is directly related to the minimum value of the d spacings included. However data at high scattering vectors are not easy to obtain either with X-rays or with neutrons. With X-rays

the problem is the fall off in the atomic structure factor with Q . For example in nickel, this is only around $\frac{1}{10}$ of its forward direction value at a Q of 10 \AA^{-1} and this residual value is not known with great accuracy. With thermal neutrons of wavelengths close to 1 \AA the maximum possible value of Q is limited to the value of about 12 \AA^{-1} obtained in the back-scattering position. It follows that for higher values of Q shorter-wavelength or epithermal neutrons must be used. If these are produced conventionally by Bragg reflexion from a monochromating crystal, there are serious problems