

Determination of the Interstitial Concentration of V in Disordered VO_{1.23} by an Intersecting Kikuchi-Line Method

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The concentration of V atoms at interstitial tetrahedral sites in VO_{1.23} above the ordering temperature has been determined through structure-factor measurements. Using an electron diffraction method which utilizes the splitting of weak Kikuchi lines near their crossing with strong bands, the 002 structure factor has been determined to within 3% accuracy. The value obtained is explained by the existence of a fraction of interstitial atoms close to that of the ordered phase. This supports the assumption that the defect cluster typical of the ordered phase persists above the ordering temperature.

Introduction

Many inorganic non-stoichiometric compounds contain large fractions of defects such as vacancies and interstitials, and a problem connected with these compounds is to determine the kind of defects present. In monoxides of the NaCl-type structure with a cation deficiency, a fraction of the cations may enter interstitial lattice positions in addition to the vacancies at the normal octahedral sites. As the intensities in the fundamental reflexions are given in terms of the occupancy of the sublattices, diffraction methods are therefore well suited to determine these fractions.

Vanadium monoxide has generally a deficiency of both vanadium and oxygen; at the composition used in the present studies, VO_{1.23}, the fractions are 19% and 1% respectively, (Banus & Reed, 1970). VO_{1.23} forms a superstructure, V₅₂O₆₄, below 800°C (Westman & Nordmark, 1960) which has been shown by Andersson & Gjønnes (1970) to result from ordering of defect clusters consisting of vanadium vacancies at the corners of a regular tetrahedron and a vanadium atom at the centre, *i.e.* in an interstitial position. The presence of such clusters above the ordering temperature also has been suggested by Andersson & Taftø (1972) from analysis of the diffuse scattering observed in electron diffraction patterns.

A fraction of vanadium atoms positioned at tetrahedral sites seems therefore to exist in the high-temperature region. These atoms can scatter out of phase with atoms at octahedral sites and thus have an influence on the size of the structure factors; in particular U_{002} is very sensitive to the presence of interstitial atoms. To investigate the interstitial fraction of vana-

dium in disordered VO_{1.23} this structure factor has been determined in the present work using the intersecting Kikuchi-line method suggested by Gjønnes & Høier (1971).

Experiments and calculations

Specimens of composition VO_{1.23} were annealed for 3 weeks at 820°C, which is 20°C above the ordering temperature, followed by a rapid quench to room temperature. The specimen-preparation technique was similar to the one used by Andersson & Gjønnes (1970), and the single crystals were studied in a Philips EM 300 electron microscope operating at 100 kV.

The diffraction patterns were taken from thicker parts of the specimen where strong multiple diffuse scattering produces a relatively homogeneous background intensity with distinct Kikuchi lines, as shown in Fig. 1(a). In the vicinity of their intersections with the strong 002 band, the weak lines are seen to be split into two segments of hyperbolic shape. Although a large number of beams are necessary to describe this contrast anomaly in detail, the effect can be described in terms of three interacting beams, and from three-beam considerations it has been shown that the gap width between the two line segments is proportional to the structure factor U_{002} when measured along the Kikuchi-band edge (Gjønnes & Høier, 1969, 1971). Referring to Fig. 1(b) one obtains for g equal to 422 and 424:

$$U_{002} = 2ks_g = \left(\frac{1}{d_g}\right)^2 \frac{h}{R_g} \sin \theta_g$$

where U_{002} is in Å⁻², k is the wave vector, s_g the excitation error and d_g the lattice-plane spacing. This expression represents a good approximation when all interacting beams are considerably weaker than 002; for

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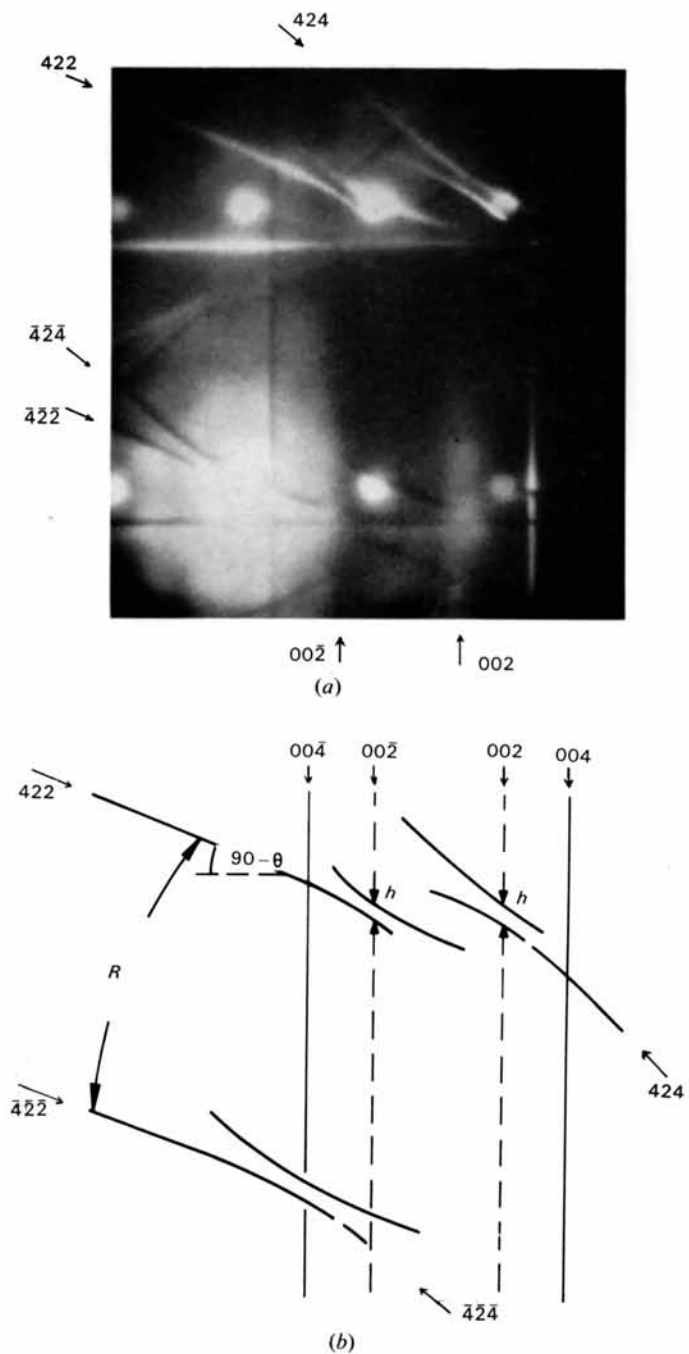


Fig. 1. (a) Transmission Kikuchi line pattern from $\text{VO}_{1.23}$ showing split lines. 100 kV. (b) Schematic drawing of observed intensity anomalies.

accurate determinations, however, more interacting beams have to be taken into account as shown below.

U_{002} has been determined from the 002, 422 and 002, 424 intersections shown in Fig. 1. These intersections have been chosen for several reasons; the 422 and 424 structure factors are considerably smaller than U_{002} , but are still large enough to give relatively strong and easily observable lines; also the number of beams necessary to calculate the different profiles is reasonable.

The separation between the two segments of a split line has been measured on both photometer traces and, mainly, enlarged prints. From measurements on several prints from the same plate and from plates taken at different diffraction conditions, the resulting accuracy in the values for the gap width was estimated to be within 3%. Care is then taken to avoid shifts in the intensity-peak position due to variations in the background scattering. In practice, this can be achieved by selecting incident-beam directions which give nearly constant background scattering across the gap between the split lines.

The measured gap width has been compared with profiles along the 002 Kikuchi-band edge calculated on basis of 12 interacting beams, which proved to be a sufficient beam number. The theoretical intensity profiles were calculated on the basis of constant diffuse background intensity. The temperature factor used in these calculations was taken to be similar to the one determined from X-ray data for the ordered phase immediately below the ordering temperature (Andersson & Gjønnes, 1970). Since the dominating parameter in the calculations is the low-index 002 structure factor an error in the temperature factor will have only a slight effect on the gap width. This applies to the uncertainties in the value of lattice parameter, composition and effects due to displacement disorder as well.

The calculations were performed with sets of structure factors corresponding to four different concentrations of interstitial vanadium atoms, ranging from $x_i = 0$ to $x_i = 4$ per unit cell of the ordered phase. The former corresponds to vacancies on the vanadium sublattice,

the latter to the number of interstitial atoms in the ordered phase where 4 of the 128 available tetrahedral sites are occupied by vanadium atoms.

For the structure factors to be used in the many-beam calculations the questions arise of the ionization states of the atoms and the model for calculation of atomic scattering factors. In the present case the ionization state is expected to be low, and the calculated gap width as a function of interstitial concentration using the preferred relativistic Hartree-Fock scattering factors due to Doyle & Turner (1968), is shown by the solid line in Fig. 2.

The calculated gap widths in Fig. 2 are normalized to unity for zero interstitial atoms giving a relative value of the measured gap as 0.91 ± 0.03 . This leads to an experimentally determined number of interstitial atoms per unit cell of 3.6 ± 1 which, within the standard deviation, corresponds to the number in the ordered V₅₂O₆₄ structure.

To include the possibility of other ionization states and also of different models for calculations of atomic

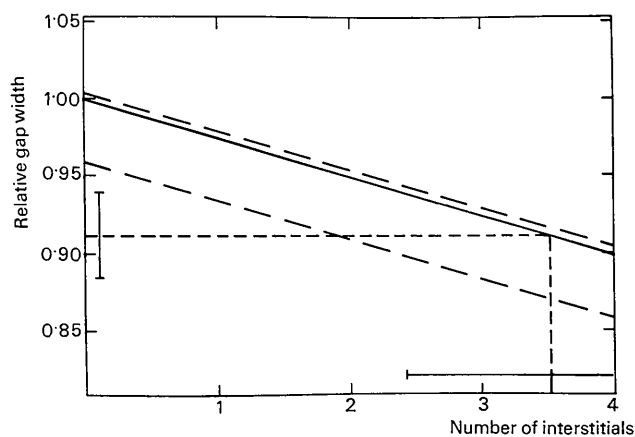


Fig. 2. Calculated relative gap width as a function of the number of interstitial atoms per unit cell.

Table 1. Extreme values of U_{002} and range of experimentally determined interstitial concentration for various models

Oxidation state	V	References	O	Experimental x_i
V ⁰ O ⁰	Cromer & Mann (1968)	Cromer & Mann (1968)		3.7
	Watson & Freeman (1961)	Hanson, Herman, Lea & Skillman (1964)		2.2
V ⁺¹ O ⁻¹	Watson & Freeman (1961)	Cromer & Mann (1968)		3.2
V ²⁺ O ²⁻	Cromer & Mann (1968)	Suzuki (1968) 1 Well		3.5
	Hanson <i>et al.</i> (1964)	Tokonami (1965)		2.0

scattering factors, a number of combinations have been used. In Table 1 the extreme values determined for neutral, single-ionized and double-ionized atoms are given. The upper and lower limits of the gap widths calculated for different x_i are shown by dotted lines in Fig. 2.

Discussion

Structure-factor determinations by X-ray powder methods were found to be too inaccurate and single crystals suitable for X-ray methods could not be obtained in the present case. Neither could neutron methods be applied because of the very small scattering amplitude of vanadium for neutrons.

With electrons the intensity in the fundamental Bragg spots cannot be utilized as in the X-ray and neutron diffraction cases, but turning to special dynamic effects, structure factors can be obtained with sufficient accuracy. The convergent-beam technique (Goodman & Lehmpfuhl, 1967) and the splitting of reflexions by wedge-shaped crystals (Lehmpfuhl, 1972) were eliminated as these methods need both very special crystal geometries and modifications to the instrument. Small single crystals producing distinct Kikuchi-line patterns are, however, easily obtained. The method suggested by Watanabe, Uyeda & Fukuhara (1968) which utilizes the disappearance of a second-order Kikuchi line at a particular voltage could not be applied as only a conventional microscope was available during the present studies.

The intersecting Kikuchi-line method used was found to be the only diffraction method giving the required accuracy in the present structure problem. This method is based on diffraction effects which can be observed in a standard microscope at any voltage, and has the further advantage that higher-order structure factors are relatively unimportant. Uncertainties due to temperature factor and static atomic displacement will consequently affect the result only to a very little extent. It should be noted that the gap width increases with voltage. The experimental error may hence be less at higher voltages while the number of beams to be used in the calculations increases.

Two contributions to the uncertainty in the present

case are from the choice of ionization state and the scattering amplitude. With the assumption that the ionization state is low the number of interstitial atoms per unit cell of the ordered phase will be 3.6 ± 1 using the scattering factors of Doyle & Turner (1968). This corresponds to the concentration in the ordered $V_{52}O_{64}$ structure. Taking different ionization states and different tabulated values for scattering factors into account, Table 1 shows that the experimentally determined concentration will be in the range from 2 to 3.7. The result is thus significantly different from the one expected for the disordered NaCl-type lattice without interstitials. The presence of interstitial vanadium atoms in $VO_{1.23}$ above the transition temperature at 800°C is therefore established, and the assumption that the phase transition is an order-disorder transition involving ordering of defect clusters is strongly supported.

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