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Determination of Structure Factors of Disordered Vanadium Monoxide Crystals by the Intersecting-Kikuchi-Line and Critical-Voltage Methods

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The concentration of vanadium atoms at interstitial tetrahedral sites in disordered $VO_{0\cdot82}$ and $VO_{1\cdot20}$ crystals has been determined by use of both the intersecting-Kikuchi-line method and the critical-voltage method. It is shown that not only the structure factor but also the temperature factor can be determined by combining the two methods. From the structure-factor values obtained, the existence of interstitial vanadium atoms is confirmed for the disordered $VO_{1\cdot20}$, supporting the assumption that the defect cluster typical of the ordered phase persists in the disordered state, whereas the interstitial concentration in the disordered $VO_{0\cdot82}$ is found to be nearly zero. For $VO_{1\cdot20}$ and $VO_{0\cdot82}$ the values of $1\cdot21 \pm 0\cdot12$ and $1\cdot05 \pm 0\cdot10$ Å^2 respectively at room temperature were obtained for the B factor which includes contributions from static atom displacements as well as the effect of thermal vibrations.

Introduction

Vanadium monoxide has a NaCl type structure with large fractions of vacancies on both metal and oxygen sites and exists over a wide range of composition from about $VO_{0\cdot8}$ to $VO_{1\cdot3}$ at 900°C (Schönberg, 1954; Andersson, 1954; Westman & Nordmark, 1960; Stenström & Westman, 1968). At the composition $VO_{1\cdot0}$ about 15% of both metal and oxygen sites are vacant; the concentrations of metal and oxygen vacancies depend on the composition. In the composition range $VO_{1\cdot17}$ to $VO_{1\cdot30}$, ordering of vacancies occurs at temperatures below 800°C. Two of the present authors (Andersson & Gjönnes, 1970) have shown that specimens with composition in the range $VO_{1\cdot20}$–$VO_{1\cdot30}$ form a tetragonal superstructure, which can be described as an ordered arrangement of defect clusters consisting of one vanadium interstitial at a tetrahedral position, surrounded by four vanadium vacancies.

The existence of such clusters also in the disordered state above the ordering temperature has been concluded recently for $VO_{1\cdot23}$ by Andersson, Gjönnes & Taftö (1974) from analysis of the short-range-order diffuse scattering in electron diffraction.

Since the interstitial vanadium atoms scatter out of phase with atoms at octahedral sites for reflexions with $h+k+l=4n+2$, the concentration of interstitial can be determined by accurate measurements of the structure factor for such reflexions. Höier & Andersson (1974) have already measured the structure factor of the 002 reflexion of disordered $VO_{1\cdot23}$ for this purpose, using the intersecting-Kikuchi-line method suggested by Gjönnes & Höier (1971). The value obtained was explained by the existence of a fraction of interstitial atoms close to that of the ordered phase, lending further support to the assumption that the defect cluster typical of the ordered phase persists above the ordering temperature.

It was found desirable to investigate whether such vanadium interstitials exist also at other compositions of the disordered state. Furthermore it is of interest to compare the intersecting-Kikuchi-line method with the critical-voltage method developed by Watanabe, Uyeda & Fukuhara (1968). Therefore, the structure factor for the 002 reflexion of disordered $VO_{0\cdot82}$ and $VO_{1\cdot20}$ has been measured using both these methods.

Either of the two utilizes multiple-beam dynamical effects in electron diffraction. The critical-voltage method uses the effect of the vanishing of the second-order reflexion at a particular accelerating voltage E_c owing to variations in multiple-beam interactions with electron mass. The structure factor for electrons for the first-order reflexion U_1 is obtained by using the measured value of E_c and known values of U_n for the second and higher-order reflexions ($n=2,3,\cdots$). The method is limited to systematic reflexions and is normally dependent on high-voltage electron diffraction. It has already been applied to a number of substances, metals and oxides, where structure factors have been obtained with an accuracy of 1–2% (Watanabe, Uyeda & Fukuhara, 1969; Watanabe & Terasaki, 1972; Fujimoto, Terasaki & Watanabe, 1972; Arii, Uyeda, Terasaki & Watanabe, 1973). There is one disadvantage, however. The temperature factor of the crystal must be known, because it has an effect upon the structure-factor value determined from the experimental value of E_c through the sizes of the structure factors of higher-order reflexions involved in the interaction. The intersecting-Kikuchi-line method, on the other

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hand, is not so dependent upon the temperature factor. Here the separation between the two split segments of a line is measured at the intersection with a strong band. From this separation, the structure factor of the strong reflexion can be determined within 2–3 % accuracy in favourable cases. An error in the temperature factor has only a slight effect on the final result, since the dominating parameter in the calculation is the low-index structure factor; by a favourable choice of line intersections, the effect of higher-order beams may almost cancel so that the structure factor at room temperature can be obtained without knowing the value of the temperature factor. This also suggests the feasibility of determining the temperature factor as well as the structure factor through the application of both methods.

Experimental

Specimens of compositions $VO_{0 \cdot 82}$ and $VO_{1 \cdot 20}$ were prepared by arc melting appropriate mixtures of vanadium metal (99·7 % pure) and V_2O_3 powder (99·7 %) under an argon atmosphere. They were melted repeatedly to ensure homogeneity in composition, then sealed in evacuated silica tubes, annealed at high temperatures for 1 week and, finally, quenched by dropping them into iced water. Annealing temperatures were 1200 and 1000 °C for $VO_{0 \cdot 82}$ and $VO_{1 \cdot 20}$ respectively. Oxygen contents of the specimens were determined by the mass change after oxidation to V_2O_5 in the atmosphere at 650 °C for 4 days. The accuracy of the analyses is estimated to ± 1 at. % oxygen.

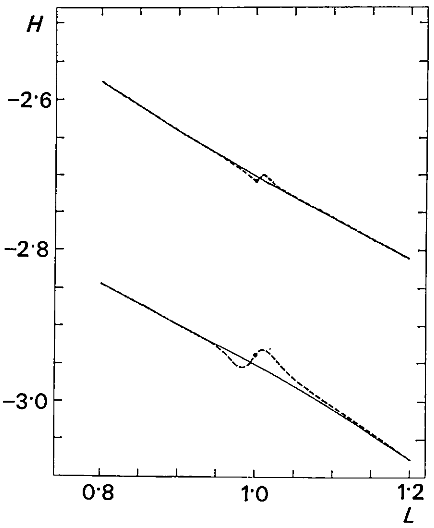

Fig. 1. Calculated positions of the split excess line near the $\bar{4}\bar{2}\bar{2}$, 002 intersection, as given by the maximum excess contrast (broken curves). The coordinates, H and L, are given in fractions of 001 and $1\frac{1}{2}0$, referred to the zone axis $[1\bar{2}0]$ as the origin. The smoothed full-line curve was used to define the separation of the split lines.

Thin slices of 3–5 mm thick were cut from the quenched specimens and then polished metallographically to approximately 0·5–1 mm thickness. These were electropolished in an electrolyte containing 5 % sulphuric acid and 95 % methanol (at 20V) or 10 % perchloric acid and 90 % methanol (at 13V). Sometimes, ion etching was applied after electropolish.

Diffraction patterns showing the 002, 422 and 002, 424 Kikuchi line intersections were taken in a Philips EM 300 electron microscope operating at 100 kV, following the experimental procedures described in the paper by Höier & Andersson (1974). The critical voltages E_c for the 004 reflexion were determined from a series of systematic Kikuchi line patterns taken at various accelerating voltages with a 500 kV Hitachi electron microscope.

Results and calculations

In the intersecting-Kikuchi-line method, the intersections between the 422 and 424 lines and the 002 band were used, as in the previous study of $VO_{1 \cdot 23}$ by Höier & Andersson (1974). The separation between the two segments of hyperbolic shape were measured, at both intersections, on enlarged prints. From a series of measurements, the random errors were estimated to ± 1 % in the average. Systematic errors, from non-zero slope of background, absorption effects *etc.* were reduced through the choice of diffraction condition (incident beam near the 422, 424 intersection) and are assumed to be less than 1 %. The measured separations, listed in Table 1, are given as excitation errors for the reflexion 002.

For comparison with the measured separations, theoretical intensity profiles of the split segments were calculated along different sections parallel to the band

Table 1. *Excitation errors and structure factors for the* 002 *reflexion determined by the intersecting-Kikuchi-line method*

	$VO_{0 \cdot 82}$		$VO_{1 \cdot 20}$	
Lattice parameter (Å)	4·025		4·122	
Occupation probabilities (%)				
Vanadium site (x_V)	89		81	
Oxygen site (x_O)	73		97	
	422	424	422	424
Excitation error ($Å^{-2}$)*	$(7 \cdot 96 \pm 0 \cdot 1) \times 10^{-2}$	$(7 \cdot 56 \pm 0 \cdot 1) \times 10^{-2}$	$(7 \cdot 04 \pm 0 \cdot 1) \times 10^{-2}$	$(6 \cdot 64 \pm 0 \cdot 1) \times 10^{-2}$
$U_{002} = \frac{2m_0e}{h^2} V_{002}$ ($Å^{-2}$)	$(6 \cdot 30 \pm 0 \cdot 1) \times 10^{-2}$	$(6 \cdot 27 \pm 0 \cdot 1) \times 10^{-2}$	$(5 \cdot 59 \pm 0 \cdot 1) \times 10^{-2}$	$(5 \cdot 62 \pm 0 \cdot 1) \times 10^{-2}$

* The factor $2k$, where k is the magnitude of the wave vector, is included in the excitation error.

edge; constant background intensity was assumed and 19 interacting beams were included in the calculation. The dotted curves in Fig. 1 show the loci of calculated intensity maxima, corresponding to the two segments of the split 422 line for $VO_{1\cdot20}$. The anomaly in the near vicinity of the band edge should be pointed out. This anomaly, which was not reported by Höier & Andersson (1974) whose calculations were restricted to the band edge, is too small in extension to be detected in the experimental pattern. Therefore, smooth curves of hyperbolic shape (full-line curves in Fig. 1) were taken to represent the theoretical line profiles to be compared with the experiment.

The values, U_{002}, of the structure factor determined from the comparison are given in Table 1. The higher-order structure factors used in the many-beam calculation were calculated from theoretical atomic scattering factors for neutral vanadium and oxygen atoms given by Doyle & Turner (1968), taking the fractions of deficiency in both vanadium and oxygen sites (Table 1) into account. Since the temperature factor of disordered vanadium monoxide was not known, the B factor of 0·7 Å^2 which has been determined for the ordered phase $VO_{1\cdot23}$ below ordering temperature (Andersson & Gjønnes, 1970) was at first assumed. It should be emphasized however, that the U_{002} values determined by this method were not very sensitive to the values used for the higher-order structure factors. This is because the effects of higher-order beams very nearly cancel for the 002, 422 and 002, 424 intersections. The error contributions to U_{002} from uncertainties in other structure factors, through the interstitial concentration, ionization degree and B factor, can therefore be neglected. Calculations in which these parameters were varied within resonable limits produced changes in the gap width amounting to less than 0·2%. Thence the 002 structure factor values at room temperature given in Table 1 can be taken as independent of these factors within the experimental accuracy; they affect the values only through their effect on the U_{002} structure factor itself.

The critical voltages E_c for the 004 reflexion were found to be 312 ± 5 and 430 ± 9 kV, respectively, for $VO_{0\cdot82}$ and $VO_{1\cdot20}$. Assuming a B factor of 0·7 Å^2, neglecting the contribution from interstitials to higher-order reflexions and using the theoretical atomic scattering factors given by Doyle & Turner, values of U_{002} at room temperature were obtained from the measured values of E_c by many-beam calculations. They were $(6\cdot631 \pm 0\cdot020) \times 10^{-2}$ and $(6\cdot055 \pm 0\cdot029) \times 10^{-2}$ Å^{-2} for $VO_{0\cdot82}$ and $VO_{1\cdot20}$ respectively, which are considerably larger than those determined by the intersecting-Kikuchi-line method. The values from the two methods should agree with each other, in so far as the same theoretical atomic scattering factors are used for the higher-order structure factors; therefore the large discrepancy was ascribed to improper choice of B factor and to neglect of the existence of interstitial vanadium atoms. These two factors affect the result in the critical-voltage method, but not in the intersecting-Kikuchi-line method.

Then, with both the B factor and the concentration of interstitial vanadium atoms as parameters, two calculations were performed. Firstly, theoretical values of the first-order structure factor,

$$U_{002} = \frac{4}{\pi v_O} \{(x_V - 4x_i)f_V + x_O f_O\} ,$$

were calculated. Here x_V and x_O are the occupation probabilities of vanadium and oxygen sublattices, as obtained from the pycnometric and X-ray density measurements (Table 1), x_i the probability of finding vanadium atom in the interstitial site, v_O the volume of disordered unit cell (NaCl type), and f_V and f_O the atomic scattering factors for electrons for vanadium and oxygen atoms, for which theoretical values of Doyle & Turner were used. Broken lines in Fig. 2 show examples of this calculation with $B = 0\cdot7$ and and 1·2 Å^2 for $VO_{1\cdot20}$. If the B factor is known, x_i can be determined directly by comparing the U_{002} value obtained by the intersecting-Kikuchi-line method with calculated values. Since this was not the case, experimental values of U_{002} were calculated from the measured value of E_c by the use of the theoretical scattering factors of Doyle & Turner for the higher-order systematic reflexions. Examples of the calcula-

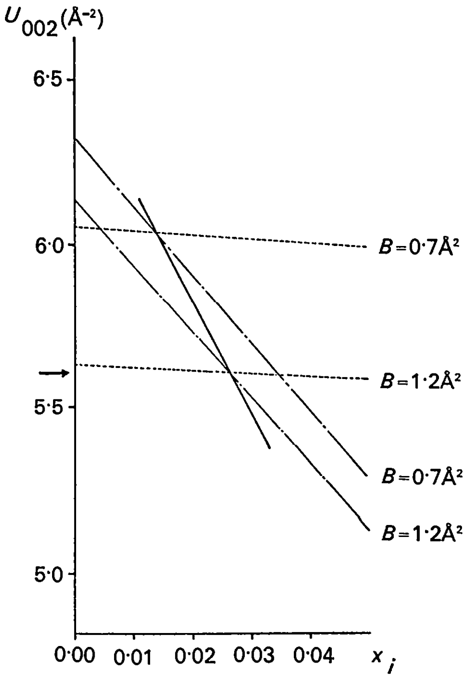

Fig. 2. Calculated and experimental values of the Fourier potential of the 002 reflexion as function of the interstitial occupancy, x_i. Broken line: calculated from tabulated atomic scattering factors for $B = 1\cdot2$ and 0·7 Å^2. Dotted line: calculated from the experimental value for E_c. Full line: locus of intersections. Arrow: value obtained from the intersecting-Kikuchi-line method.

tions are given as dotted lines in Fig. 2. From the intersection of this line with the corresponding broken line, the interstitial concentration x_i for a particular B value is found. A full line shows the locus of such intersections. The best agreement between the results by the two experimental methods is obtained for the B factor of 1·21 Å². With the experimental error in the U_{002} value determined by the intersecting-Kikuchi-line method taken into account, the following results are obtained for $VO_{1\cdot20}$:

$$B=1\cdot21\pm0\cdot12\ \text{Å}^2,\quad x_i=0\cdot026\pm0\cdot005\ .$$

Similar analysis for $VO_{0\cdot82}$ gives the results:

$$B=1\cdot05\pm0\cdot10\ \text{Å}^2,\quad x_i=0\cdot004\pm0\cdot003\ .$$

If the interstitial concentration is expressed in terms of the number of interstitial atoms X_i in the lattice corresponding to the ordered $V_{52}O_{64}$ unit cell, the X_i values obtained for $VO_{1\cdot20}$ and $VO_{0\cdot82}$ correspond to 3·3 ± 0·6 and 0·5 ± 0·4 respectively.

In order to include the possibility of other ionization states and also of different models for calculations of atomic scattering factors, we performed similar calculations by the use of theoretical atomic scattering factors given by Fukamachi (1971) for neutral atoms (V^0,O^0), positive ions (V^{1+},V^{2+}) and the monovalent oxygen ion (O^{1-}) and those given by Sanger (1969) for the divalent ion (O^{2-}). Results of such calculations for $VO_{1\cdot20}$ are reproduced in Fig. 3, in which the loci of possible combinations of B and x_i, corresponding to the full line of Fig. 2, are plotted in a (x_i, B) graph. The intersection of the x_i value and error limits with the line yield B factors and error limits for the particular model, as indicated in the figure. The results for both compositions are summarized in Table 2. It should be pointed out that the analysis based upon ionized atoms lead to negative values for the interstitial concentration in $VO_{0\cdot82}$, which of course is meaningless. This suggests that the atoms, at least in the metal-rich oxide, are neutral.

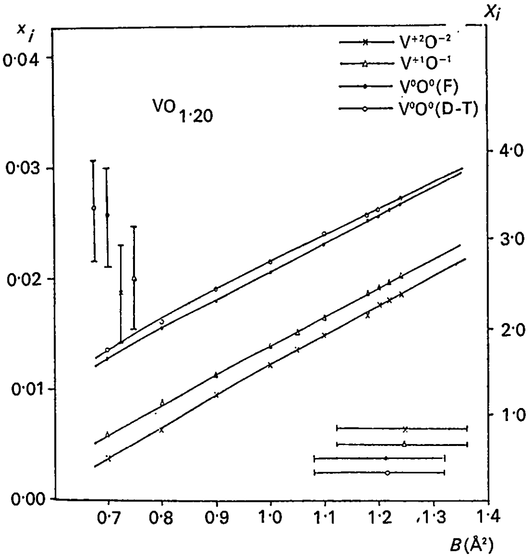

Fig. 3. Calculated values of the interstitial fraction as function of the temperature factor B for the four sets of atomic scattering factors given in Table 2, as indicated by different markings. The interstitial fraction is given as the occupancy x_i and the number of interstitials X_i in an ordered unit cell. Vertical lines are the error limits derived from Fig. 2 and horizontal lines the resulting B values with error limits.

Discussion

In electron diffraction it is usually very difficult to obtain structure factors and the temperature factor from the measurement of spot intensities, in contrast with the X-ray and neutron diffraction cases. However, in the last few years, several experimental methods which exploit multiple-beam dynamical effects for determination of structure factors have been developed. Among them, those like the critical-voltage and intersecting-Kikuchi-line methods are more widely applicable to normal electron-diffraction specimens since large crystals with special geometries are not required; small crystals which produce distinct Kikuchi-line patterns in selected-area diffraction are adequate. In particular, the low-index structure factors for a number of metals have been determined by the critical-voltage method with an accuracy as good as that of the most reliable X-ray measurements. Unfortunately the application of this method may be limited to crystals whose temperature factors are known.

In the present study we have shown that a combination of the intersecting-Kikuchi-line and critical-voltage methods can be used to determine both a low-index structure factor and the temperature factor. Such a combination appears particularly useful in the present case, where one low-index structure factor, U_{002}, is quite sensitive to an essential element in the structure, *viz*, the concentration of metal atoms at tetrahedral sites. It may be noted that the methods thus have been applied to a system which includes substitutional long- and short-range order, that is to a system which may

Table 2. *The B factors at room temperature and the number of interstitial vanadium atoms in the lattice corresponding to the ordered unit cell*

Atomic states	References V	References O	B Factor (Å²) $VO_{0\cdot82}$	B Factor (Å²) $VO_{1\cdot20}$	The number of interstitials $VO_{0\cdot82}$	The number of interstitials $VO_{1\cdot20}$
V^0 O^0	Doyle & Turner (1968)		1·05 ± 0·10	1·21 ± 0·12	0·5 ± 0·4	3·3 ± 0·6
	Fukamachi (1971)		1·06 ± 0·10	1·21 ± 0·12	0·4 ± 0·4	3·3 ± 0·6
$V^{1+}O^{1-}$	Fukamachi (1971)		1·08 ± 0·10	1·24 ± 0·12	–	2·4 ± 0·6
$V^{2+}O^{2-}$	Fukamachi (1971)	Sanger (1969)	1·08 ± 0·10	1·24 ± 0·12	–	2·6 ± 0·6

be typical of structure problems studied by electron diffraction.

The errors in the determination of the Fourier potential U_{002}, the interstitial concentration x_i and the temperature factor B can be discussed with reference to Fig. 2. U_{002} is determined by the intersecting-Kikuchi-line method essentially independently of x_i and B with error limits directly related to the uncertainty in the measurement of line separation. The error in the measurement of critical voltage is much smaller therefore; the errors in B and x_i are given by a combination of the error in U_{002} and the slope of the full line in Fig. 2 or in Fig. 3. It should be mentioned that the accuracy may be improved if the intersecting-Kikuchi-line patterns are taken at a higher accelerating voltage since the separation of the split line increases with voltage, as shown by Höier (1971).

The B factors obtained for vanadium monoxide at room temperature in the present study may be considered to be remarkably large for a transition-metal oxide. It should be pointed out, however, that they include the effect of static atomic displacements near vacancies and interstitial atoms as well as of thermal vibrations; the former effect may contribute significantly to the measured B factors at room temperature.

The concentration of interstitial vanadium atoms estimated for $VO_{1.20}$ through structure-factor measurement agrees well with the value for $VO_{1.23}$ obtained in the previous study by Höier & Andersson (1974). Even if the uncertainties arising from the choice of ionization state and the theoretical scattering-factor values used in the calculation are taken into account, it can be safely concluded that the disordered oxygen-rich oxide $VO_{1.20}$ contains a fraction of interstitial vanadium atoms close to that of the ordered phase.

The result for the metal-rich oxide $VO_{0.82}$ is significantly different: The concentration of interstitial atoms was found to be nearly zero for this composition, although the concentration of vanadium vacancies decreases only by a factor of two on going from $VO_{1.20}$ to $VO_{0.82}$ (Table 1). It is also worth noting that only the analysis based on the neutral atoms gives a reasonable solution for $VO_{0.82}$, suggesting that the elements are not in the ionized states at least in the vanadium-rich oxide. This is similar to what was found for metal-rich titanium monoxides through structure-factor determination by the critical-voltage method (Watanabe & Terasaki, 1972).

Measurement of critical voltage was carried out by using a 500 kV electron microscope in the Institute for Solid State Physics, University of Tokyo. The authors wish to thank the ISSP for giving them opportunities of using the equipment. They are indebted to Mr K. Suzuki and Mr M. Ichihara of ISSP for their help in the experiment, and to Mr K. Ohshima of Tohuku University for his aid in specimen preparation.

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References

ANDERSSON, G. (1954). *Acta Chem. Scand.* **8**, 1599–1606.

ANDERSSON, B. & GJÖNNES, J. (1970). *Acta Chem. Scand.* **24**, 2250–2252.

ANDERSSON, B., GJÖNNES, J. & TAFTÖ, J. (1974). *Acta Cryst.* A**30**, 216–224.

ARII, T., UYEDA, R., TERASAKI, O. & WATANABE, D. (1973). *Acta Cryst.* A**29**, 295–298.

DOYLE, D. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

FUJIMOTO, M., TERASAKI, O. & WATANABE, D. (1972). *Phys. Letters*, **41**A, 159–160.

FUKAMACHI, T. (1971). *Tech. Rep. ISSP ser. B*, No. 12. The University of Tokyo.

GJÖNNES, J. & HÖIER, R. (1971). *Acta Cryst.* A**27**, 313–316.

HÖIER, R. (1971). 2nd Int. Conf. on High-Voltage Electron Microscopy. *Jernkont. Ann.* **155**, 472–473.

HÖIER, R. & ANDERSSON, B. (1974). *Acta Cryst.* A**30**, 93–95.

SANGER, P. L. (1969). *Acta Cryst.* A**25**, 694–701.

SCHÖNBERG, N. (1954). *Acta Chem. Scand.* **8**, 221–225.

STENSTRÖM, G. & WESTMAN, S. (1968). *Acta Chem. Scand.* **22**, 1712–1714.

WATANABE, D. & TERASAKI, O. (1972). *Solid State Chemistry, NBS Special Publication* 364, *Proceedings of 5th Materials Research Symposium*, edited by R. S. ROTH and S. J. SCHNEIDER, pp. 155–164.

WATANABE, D., UYEDA, R. & FUKUHARA, A. (1968). *Acta Cryst.* A**24**, 580–581.

WATANABE, D., UYEDA, R. & FUKUHARA, A. (1969). *Acta Cryst.* A**25**, 138–140.

WESTMAN, S. & NORDMARK, C. (1960). *Acta Chem. Scand.* **14**, 465–470.