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Neutron Diffraction Measurement of Diffuse Scattering in VC$_{0\cdot75}$

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The location of diffuse intensity originally observed in electron diffraction patterns of short-range-ordered VC$_{0\cdot75}$, has been confirmed by neutron diffraction experiments on a four-circle diffractometer. A new set of short-range order parameters has been calculated on the basis of these accurate intensity data and the agreement between experimental results and theoretical predictions for short-range-ordered compounds with NaCl related structure has been improved.

Introduction

Non-stoichiometric vanadium carbide $VC_{x_C}\square_{x_\square}$ has been extensively studied by electron microscopy (Billingham, Bell & Lewis, 1972). Diffuse intensity is observed on electron diffraction patterns and has been attributed to short-range order in the carbon vacancy distribution. The diffuse intensity surface (Fig. 1) is approximately described by the equation

$$\cos \pi h_1 + \cos \pi h_2 + \cos \pi h_3 = 0 \qquad (1)$$

(h_1, h_2 and h_3 being continuous variables in reciprocal space) which was shown to be characteristic of short-range order in NaCl derivative structures (Sauvage & Parthé, 1974). A calculation of Warren short-range order parameters has been performed on the basis of electron diffraction patterns (Sauvage & Parthé, 1972). Theoretical predictions based on N.M.R. data obtained by Froidevaux & Rossier (1967) indicate that in the particular compound under investigation, VC$_{0\cdot75}$, the first three short-range order parameters should fulfill the equation (Sauvage & Parthé, 1974)

$$\alpha_0 + 4\alpha_1 + \alpha_2 = 0\cdot22 \, . \qquad (2)$$

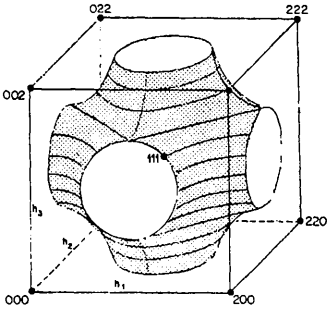

Fig. 1. Model for the diffuse intensity surface according to equation (1).

However, the parameter values obtained from the electron diffraction patterns lead to 0 instead of 0·22. It was therefore decided to measure this diffuse intensity more accurately by neutron diffraction. The use of neutrons provides direct evidence that the diffuse intensity is actually related to short-range order of the *carbon* vacancies, since the vanadium contribution to the coherent scattering is almost negligible. A preliminary experiment (Sauvage & Parthé, 1973) indicated that this technique was appropriate to the problem.

Experimental

The sample used for the measurements was a single crystal of cylindrical shape (height: 2mm, diameter: 8mm) whose composition was VC$_{0\cdot75}\square_{0\cdot25}$ with $a = 4\cdot13$ Å.

The experiment was performed on the D10 four-circle neutron diffractometer located on the thermal neutron guide *H*-24 at the Institute Laue Langevin. A Cu(111) monochromator was used at an incident wavelength $\lambda = 1\cdot44$ Å. The $\lambda/2$ component arriving at the sample position was determined to be 0·2% of the λ component. Flux at the sample position was about 6×10^5 n cm^{-2} sec^{-1}. The guide provides at this wavelength, collimation (horizontal and vertical) of about 12′. After the monochromator the beam was defined by two diaphragms. No collimation was used after the sample.

The instrument is piloted by a Telemechanique 2000 computer (Carine 1) which is programmed in Fortran. It was therefore a simple task to choose scans in completely general directions in reciprocal space as opposed to the usual ω or ω–2θ scans used for structural crystallography. The crystal was oriented as for a standard crystallographic study and a general orientation matrix was determined.

Since the diffuse intensity surface is invariant under the symmetry operations of the body-centred space group *Im*3*m* it is necessary to explore only 1/96th of the entire surface. The section chosen for the experi-

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ment (Fig. 2) corresponds to a 2θ range from 20 to 35°. This range has been selected to avoid spurious effects such as diffraction rings due to the aluminum support for the crystal. Measurements were made along 38 scan paths of 13 steps each falling on straight lines in reciprocal space, and cutting normally through the theoretical surface given by equation (1) at the mid-point M_0. The width of each scan was $0\cdot48|a^*|=0\cdot115$ Å^{-1}.

The 38 points were distributed regularly on the surface section to be explored and were chosen by stepping h_2 and h_3 (within allowed limits) and calculating h_1 to satisfy (1). The ability to perform general scans means that at no time does the scan cut the surface tangentially (or nearly so), which would produce broad, poorly defined peaks. As the signal to noise ratio was about 1:4 owing to the incoherent vanadium background, a large counting time of 11 min per point was required. The background was also determined in the same 2θ range.

Experimental results

A large aperture was selected for the detector to optimize the signal-to-noise ratio. Consequently the resolution ellipsoid was not small with respect to the extension of the diffuse intensity in reciprocal space. The distortion introduced in the intensity values by resolution effects was calculated on the basis of a simple model for the diffuse scattering: the distribution was assumed to be Gaussian and to depend for each scan only on the distance from the maximum, which means that the equal-intensity surfaces are locally approximated by their tangent plane. The exact position of the maximum was determined on each scan and, as will be discussed in the next section, it did not always coincide with the mid-point of the scan (a possible shift of the maximum due to resolution effects was not taken into account). The resolution function has been calculated at each nominal measurement position according to the formulae given by Cooper & Nathans (1968) with the help of a program provided by one of us (W.B.Y.).

The corrected intensity values show for each scan a maximum located either on the mid-point M_0 [Fig. 3(*a*)] or slightly shifted for scans close to the diagonal plane [Fig. 3(*b*)]. This is in agreement with our previous results (Sauvage & Parthé, 1972) which showed that the experimental surface was not exactly described by (1), a correcting term being needed:

$$\cos \pi h_1 + \cos \pi h_2 + \cos \pi h_3 \\ + \; 3C_{111} \,.\, \cos \pi h_1 \,.\, \cos h\pi_2 \,.\, \cos \pi h_3 = 0\,. \quad (3)$$

On the basis of electron diffraction data, C_{111} was given the value $-0\cdot85$ and the present experiment leads to $-0\cdot65$.

The intensity of the maximum is not constant but shows an enhancement in the diagonal plane (Fig. 3). There is also a pronounced increase toward the point $\frac{1}{2},\frac{3}{2},\frac{1}{2}$ in reciprocal space; however this might be due to the tail of the 131 reflexion of $\lambda/2$ which is still higher than the diffuse scattering, or to some local long-range order of the carbon vacancies due to sample inhomogeneities.

Short-range order parameters

The Warren short-range order parameters are related through a Fourier transform to the diffuse intensity:

$$\alpha_n = \frac{1}{V^*} \int_{V^*} I(\mathbf{H}') \,.\, \exp 2\pi i(\mathbf{r}_n \,.\, \mathbf{H}')]\mathrm{d}V^* \qquad (4)$$

where $\mathbf{r}_n$ is a vector of the direct structure, $\mathbf{H}'$ any vector in reciprocal space and V^* the volume of the reciprocal unit cell.

The α_n are expressed in term of the probabilities $p_n^{\square C}$ of finding a vacancy–carbon atom pair separated by the vector r_n through the formula:

$$\alpha_n = 1 - \frac{p_n^{\square C}}{x_C}\,. \qquad (5)$$

The α_n parameters corresponding to the first coordination shells around a vacancy have been calculated according to equation (4) on the basis of the corrected intensities. The normalizing condition $\alpha_0 = 1$ was used.

The values are listed in Table 1 with the previous set calculated from electron diffraction data. Apart from α_1 the present values are consistently lower than the previous ones. This is easily understandable since the latter were obtained with an infinitely sharp scattering distribution on the surface given by equation (3), whilst the former are related to the actual distri-

Table 1. *Values of the X_n parameters*

α_n	Present determination	Previous determination*
α_1	$-0\cdot17 \pm 0\cdot005$	$-0\cdot17$
α_2	$-0\cdot20 \pm 0\cdot01$	$-0\cdot30$
α_3	$+0\cdot15$	$+0\cdot18$
α_4	$-0\cdot03$	$+0\cdot01$
α_5	$+0\cdot04$	$+0\cdot06$
α_6	$-0\cdot08$	$-0\cdot11$
α_7	$-0\cdot05$	$-0\cdot10$
α_8	$+0\cdot05$	$+0\cdot18$

* Sauvage & Parthé (1972)

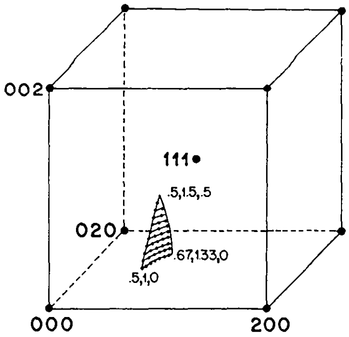
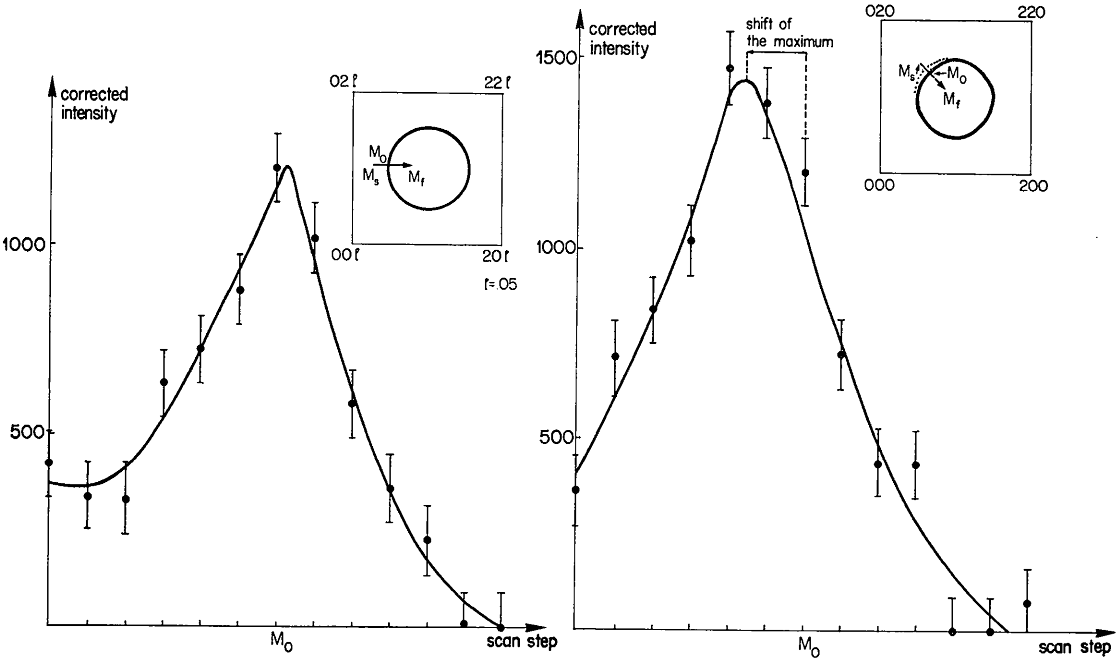


Fig. 2. Distribution of the 38 M_0 points on the fraction of the intensity surface selected for the measurements.



(*a*) (*b*)

Fig. 3. Scan profiles of neutron diffraction measurements. (*a*) Scan profile showing a maximum very close to the mid point M_0. Starting point: $M_s(h_s=0{\cdot}265,\ k_s=1{\cdot}086,\ l_s=0{\cdot}013)$; Mid-point: $M_0(h_0=0{\cdot}5,\ k_0=1{\cdot}05,\ l_0=0{\cdot}05)$; Final point: $M_f(h_f=0{\cdot}734,\ k_f=1{\cdot}013,\ l_f=0{\cdot}086)$. (*b*) Scan profile with a shift of the maximum. $h_s=0{\cdot}455$, $k_s=1{\cdot}459$, $l_s=0{\cdot}0$; $h_0=0{\cdot}635$, $k_0=1{\cdot}299$, $l_0=0$ $h_f=0{\cdot}814$, $k_f=1{\cdot}14$, $l_f=0$. In the upper right corner of each drawing is represented the location of the scan path with respect to the section of the surface. In (*b*), the section of the surface given by equation (3) is indicated with dotted lines to show that the observed shift of the maximum is in agreement with the previous estimations. The corrected intensities are given in arbitrary units.

bution which is somewhat broader, indicating a shorter range of order.

Expression (2) takes on the value:

$$\alpha_0+4\alpha_1+\alpha_2=1-4\,.\,0{\cdot}17-0{\cdot}2=0{\cdot}12$$

which represents an significant step toward the theoretical value 0·22. The remaining discrepancy may be due to two factors: first, the background may have been overestimated and some part of the diffuse scattering not included in the calculation of the α_n; second, the theory assumes that the crystal is perfectly homogenous; however, if different composition domains are diffracting independently this assumption is not fulfilled and relation (2) is no longer valid. The errors in the determination of the first α_n parameters have been roughly estimated by the effect of changing all the intensity values by one standard deviation. α_1 is quite stable and thus the value of expression (2) is not significantly affected.

Conclusion

The present experiment has confirmed that the diffuse scattering was related to short-range order of carbon vacancies and enabled a quantitative estimation of the diffuse intensity whose level is extremely low with respect to the Bragg peaks (about 1/5000th of the peak intensity). The details of the diffuse-scattering surface, as observed by electron microscopy have been exactly reproduced by the neutron diffraction measurements. The accuracy of the experiment might still be improved by working on NbC_{1-x} or TaC_{1-x} samples which show the same type of diffuse scattering but for which the level of incoherent background, here due to vanadium, would be much reduced.

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