

The value of  $M_{\text{abs}}$  would tend to be near zero for random phases and of order unity for correct phases. In practice correct sets of phases are found to give values of  $M_{\text{abs}}$  in the range about 1.0–1.4. While some incorrect sets of phases can also give values of  $M_{\text{abs}}$  of this magnitude it is unlikely that correct phases would give  $M_{\text{abs}}$  as low as 0.7, say. It should be stressed that no theoretical relationship has been found between  $M_{\text{abs}}$  and the probability of a set of phases being correct and that quoted judgments of the significance of values of  $M_{\text{abs}}$  are based on present experience – as yet limited.

Table 4 shows the value of  $M$  as 1.13 for the correct set of phases for raffinose (Berman, 1970) a trial structure for trying out methods.

Provision is made in *FASTAN* for the input of starting phases from cards. This is particularly useful when a recycling procedure is being used in which a number of phases have been calculated from a partial structure and are to be used as a basis for further phase determination. In this case it is advisable to fix most of the input phases for the initial stages of phase determination. This ensures that the new phases determined conform to the input information before refining all the phases together. If the input phases are allowed to refine immediately it is not uncommon for

them to change their values completely so they bear no relation to those input.

We wish to express our gratitude to the North Atlantic Treaty Organization for supporting liaison between our laboratories and also to the Science Research Council for its continuing support of our activities in York. We also wish to give thanks to the referee whose constructive criticisms of the first version of this paper led to a number of improvements in the presentation of the material.

#### References

- BERMAN, H. M. (1970). *Acta Cryst.* **B26**, 290.  
 COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1.  
 EVRARD, G. (1971). *Acta Cryst.* Submitted for publication.  
 GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* **B24**, 91.  
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274.  
 HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. A.C.A. Monograph No. 3.  
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.  
 KLUG, A. (1958). *Acta Cryst.* **11**, 515.  
 WOOLFSON, M. M. (1956). *Acta Cryst.* **9**, 804.

*Acta Cryst.* (1971). **A27**, 376

### Short-Range Ordering of Vacancies and Fermi Surface of TiO

BY J. R. CASTLES,\* J. M. COWLEY† AND A. E. C. SPARGO

*School of Physics, University of Melbourne, Parkville, Victoria 3052, Australia*

(Received 26 August 1970)

The structure of the disordered (high-temperature) phase of titanium monoxide has been studied by electron diffraction. Composition-dependent complex distributions of diffuse scattering are observed and interpreted in terms of short-range-ordered configurations of lattice vacancies. The proposition that the form of the diffuse scattering may correspond to ordering under the influence of long-range electronic energy terms and so show a direct relationship to the topology of the Fermi surface is examined.

#### Introduction

The titanium monoxide phase has statistically the NaCl type structure at high temperatures and is stable over a wide composition range *e.g.* from  $\text{TiO}_{0.70}$  to  $\text{TiO}_{1.25}$  at 1400°C and from  $\text{TiO}_{0.90}$  to  $\text{TiO}_{1.25}$  at 900°C and lower temperatures. The structure contains a large proportion of vacancies of both titanium and oxygen,

the relative number of each type depending on composition. For  $\text{TiO}_{1.0}$  15% of both kinds of site are vacant while  $\text{TiO}_{1.25}$  has all oxygen sites full but 22% of the titanium sites empty.

Below a certain composition-dependent critical temperature, varying from 990°C for  $\text{TiO}_{1.0}$  to about 750°C for  $\text{TiO}_{1.25}$ , super-lattice structures are formed by the ordering of vacancies. These have been analysed by Watanabe, Castles, Jostsons & Malin (1967) and Watanabe, Terasaki, Jostsons & Castles (1968, 1969) on the basis of electron diffraction single-crystal patterns and by Hilti (1968) using X-ray diffraction patterns taken from crystals having a single orientation with respect to the basic NaCl-type structure but com-

\* Present address: Department of Chemistry, University of Kansas, Lawrence, Kansas, 66044, U.S.A.

† Present address: Physics Department, Arizona State University, Tempe, Arizona 85281, U.S.A.

plicated by the twinning effects of the vacancy ordering.

Electron diffraction patterns from samples quenched from temperatures above the critical temperature show diffuse scattering of very complicated form which may be attributed to a short-range ordering of vacancies although in this case the classification of the ordering as 'short-range' represents an extension of normal usage since it is clear from the sharpness of the features in the diffraction patterns that the ordering correlation extends over distances of the order of 100 Å.

In this paper we examine this diffuse scattering in some detail, showing that it bears no more than a remote resemblance to the patterns of sharp spots given by the ordered superlattice structures. We then examine the proposition that the form of this diffuse scattering may correspond to ordering under the influence of long-range electronic energy terms and so shows a direct relationship to the form of the Fermi surface for disordered TiO (Cowley, 1969).

### The ordered superlattice structures

Firstly, in order to facilitate discussion of the disordered structures, we summarize the information available on the three types of ordered superlattice structure forming below the critical temperature. Since these structures are all based on the NaCl-type lattice, with only minor distortions, indices based on this fundamental unit cell will be used throughout.

The ordered TiO structure exists as a single-phase region from  $\text{TiO}_{0.90}$  to  $\text{TiO}_{1.10}$ . The superlattice is monoclinic and may be described in terms of vacancy ordering on every third atomic plane normal to the [110] direction. Within these planes half the titanium and half the oxygen sites are vacant in a regular, alternating array (Watanabe *et al.*, 1967). The electron diffraction pattern from the (001) orientation of  $\text{TiO}_{1.0}$  is shown in Fig. 1. The high symmetry of the superlattice spots results from the superposition of patterns from a large number of small regions having a twinned relationship in which the fundamental NaCl-type lattice orientation is maintained but the superlattice forms by vacancy ordering on different equivalent sets of {110} planes.

The  $\text{TiO}_{1.25}$  superlattice structure exists as a single phase over a very narrow range of composition. It is tetragonal and isostructural with  $\text{Au}_4\text{Mn}$  and  $\text{Ni}_4\text{Mo}$ . The oxygen sublattice is full. It is the distribution of titanium atoms and vacancies on the titanium sublattice which may be associated with the distribution of Au and Mn atoms, respectively, in the  $\text{Au}_4\text{Mn}$  structure (Watanabe *et al.*, 1968).

The electron diffraction pattern from the (001) orientation of  $\text{TiO}_{1.25}$  is shown in Fig. 2. The multiplicity of superlattice spots again results from a twin relationship between small regions in which vacancies order on equivalent {120} planes.

In the range of composition  $\text{TiO}_{1.1}$  to  $\text{TiO}_{1.25}$  there is a two-phase region with an intergrowth of very

small regions of  $\text{TiO}_{1.0}$  and  $\text{TiO}_{1.25}$ , sometimes only 20 Å in one dimension (Watanabe *et al.*, 1969).

In addition there is what has been called the 'transition' structure, reported for the case of  $\text{TiO}_{0.67}$  by Watanabe (1965), which appears to represent an intermediate stage of ordering between  $\text{TiO}_{1.0}$  and the high-temperature disordered phase. It has now been observed over the whole range of composition from  $\text{TiO}_{0.9}$  to  $\text{TiO}_{1.25}$  under conditions for which incomplete ordering seems reasonable, often in conjunction with either the  $\text{TiO}_{1.0}$  or  $\text{TiO}_{1.25}$  superlattice structure. The transition structure appears to be stable for a small temperature range near the disordering transition temperature. The vacancies appear to be ordered to the extent that they are concentrated on every third atomic plane normal to [110], but appear to be randomly arranged within these planes. The (001) electron diffraction pattern from this structure is shown in Fig. 3.

### Experimental

Bulk specimens were prepared by melting together charges of iodide titanium and high purity  $\text{TiO}_2$  in an argon-atmosphere arc furnace. The  $\text{TiO}_2$  had previously been sintered at 900°C for 12 hours in an oxygen atmosphere.

The cast alloys were inverted and remelted several times and then further homogenized by heat treatment at 1400°C for about 10 hours in an argon atmosphere. In the case of  $\text{TiO}_{1.0}$ ,  $\text{TiO}_{1.19}$  and  $\text{TiO}_{1.25}$  specimens, the composition calculated from the relative weights of the reactants was checked by oxidizing parts of each homogenized alloy to  $\text{TiO}_2$  and measuring the gain in weight. The composition could then be determined with an accuracy of 0.2 at.% oxygen. For samples of  $\text{TiO}_{1.05}$  and  $\text{TiO}_{1.09}$  this check on composition was not made and the error in oxygen content could be as high as  $\pm 0.5\%$ .

Samples of disordered TiO were prepared either by heating in a levitation furnace and quenching from the melt into a copper mould or else by heating in a resistance furnace and water-quenching from 1200 to 1400°C. In spite of the rapidity of the quenching, diffraction evidence showed that the ordered transition structure tended to form unless samples were quenched from several hundred degrees above the critical temperature. This is confirmed by Hilti (1968) who obtained evidence of the transition structure in his X-ray diffraction patterns even after quenching  $\text{TiO}_{1.0}$  samples from as high as 1200°C.

The use of quenched specimens therefore is unsatisfactory in that the diffraction patterns obtained do not correspond to the equilibrium state at any particular temperature. It may be assumed only that if no superlattice spots appear, the patterns represent the state of disorder existing in some range above the critical temperature.

In order to avoid this difficulty it would be necessary to use more rapid quenching techniques or else

observe the diffraction patterns at temperature. For this latter purpose X-ray diffraction single-crystal studies would be necessary since the small specimens used for electron diffraction oxidize rapidly at high temperatures. In either case the thermal diffuse scattering would be intense.

After quenching the bulk samples, slices 1 mm thick were cut using a spark etcher. These were metallographically polished to a thickness of about 0.2 mm and then chemically etched in a solution of 33% hydrofluoric acid, 50% nitric acid and 17% water until the edges were thin enough for electron microscopy.

The specimens were examined in a JEM-7A electron microscope operating at 100 kV. Electron diffraction patterns, representing almost planar sections of the distribution of scattering power in reciprocal space, were obtained for many different orientations each of several compositions from  $\text{TiO}_{1.0}$  to  $\text{TiO}_{1.25}$  in order to establish the three-dimensional distribution of diffuse scattering power and its variation with composition.

### The diffuse scattering distributions

Electron diffraction patterns taken from several orientations of crystals of composition  $\text{TiO}_{1.0}$ ,  $\text{TiO}_{1.19}$  and  $\text{TiO}_{1.25}$  are shown in Figs. 4, 5 and 6. Comparison with the patterns from the ordered superlattices, Figs. 1, 2 and 3, immediately reveals the interesting situation that the diffuse scattering from the disordered samples shows little relation to the positions of the superlattice spots from the ordered materials of the same composition. Thus the short-range ordering correlations existing above the critical temperature are not merely truncated forms of the long-range correlations existing in the superlattices at lower temperatures.

The (001) pattern from disordered  $\text{TiO}_{1.0}$ , Fig. 4(a), shows a diffuse maximum at the 110 position, extended along the  $\langle 110 \rangle$  directions, in place of the four spots around the 100 position in Fig. 1. Correspondingly the (110) pattern, Fig. 4(b), shows diffuse streaks along  $\langle 110 \rangle$  directions peaking at 110 and 001 positions. For consistency with these observations, weak diffuse lines should appear at the 100 positions in the (001) pattern, corresponding to the section of a thin disc of scattering power perpendicular to the [100] direction, but this line is extremely weak and, while visible on the original plate, does not appear on the reproduction.

The other prominent features of this (001) pattern are arcs joining pairs of diffuse spots which lie near the positions of the four sharp spots about the 100 position in Fig. 1.

A partial structural interpretation of the short-range ordered configuration is suggested by analogy with the ordered superlattice structure. The streaks through the 110 positions suggest a concentration of vacancies on  $\{110\}$  planes but without the regular three-plane sequence of the ordered lattice. The diffuse arcs around the 100 positions presumably indicate some ordering

of vacancies within these planes but a detailed analysis awaits a more quantitative study of the diffuse intensity distribution.

A completely different configuration of diffuse scattering is given by  $\text{TiO}_{1.25}$ . In the (001) pattern, Fig. 6(a), the streaks through the 100 positions are missing but now, around these positions, there are two parallel streaks normal to the [100] direction. In the (110) and (111) patterns, Fig. 6(b) and (c), equivalent streaks form the sides of oval shaped loops, bridged at the ends by diffuse maxima. These streaks are sections of pairs of parallel thin discs of diffuse scattering power with the space between them bridged at four corner points. In the (001) pattern, Fig. 6(a), the Ewald sphere passes between the two discs about the 110 position and cuts only the four bridges, giving the four diffuse maxima around the 110 position.

These diffuse bridges could arise from a tendency for vacancies to concentrate on (110) planes, as in the ordered  $\text{TiO}_{1.0}$  structure, but with an irregular spacing of the planes such that the average separation differs from that in ordered  $\text{TiO}_{1.0}$ . The parallel discs of scattering suggest that, within these (110) type atomic planes, the vacancies tend to form uncorrelated linear arrays in  $\langle 001 \rangle$  directions with fairly regular discontinuities in the lines of vacancies, the form of the discontinuities being that of a 'bad' anti-phase domain boundary in a face-centred cubic ordered alloy (see e.g. Moss, 1966).

The only apparent connexion between the diffuse scattering of Fig. 6(a) and the pattern (Fig. 2) from the ordered material of the same composition, is that the sharp spots of Fig. 2 lie close to, but not on, the pairs of parallel streaks about the 100 positions.

For the other compositions studied, the diffuse scattering is similar to that for  $\text{TiO}_{1.25}$  but with a progressive change in the dimensions and relative intensities of the features with composition. The similarity with  $\text{TiO}_{1.25}$  rather than with  $\text{TiO}_{1.0}$  persists not only for  $\text{TiO}_{1.19}$  which forms two-phase mixtures at low temperatures, but also for  $\text{TiO}_{1.05}$  and  $\text{TiO}_{1.09}$  for which the ordered structures follow that of  $\text{TiO}_{1.0}$ .

As the oxygen percentage decreases the  $\text{TiO}_{1.25}$  pattern is modified. The twin discs of scattering power around the 100 positions come closer together and the four diffuse spots about the 110 position, corresponding to the bridges between the discs, become stronger and sharper. These changes are clearly seen in the patterns [Fig. 5(a) and (b)] given by  $\text{TiO}_{1.19}$ .

As the  $\text{TiO}_{1.0}$  composition is approached, the separation of the twin discs of scattering decreases to zero to give, as a limiting case, the streak through 100 observed for  $\text{TiO}_{1.0}$ . Notably, the arcs around the 100 positions occurring in  $\text{TiO}_{1.0}$  patterns are not seen for other compositions.

The form of the diffuse scattering for each composition is sketched in Fig. 7 and the progressive change in the dimensions indicated in that Figure is shown by the measurements recorded in Table 1.



Fig. 1. (001) diffraction pattern of ordered  $\text{TiO}_{1.0}$  showing superposition of many orientations.

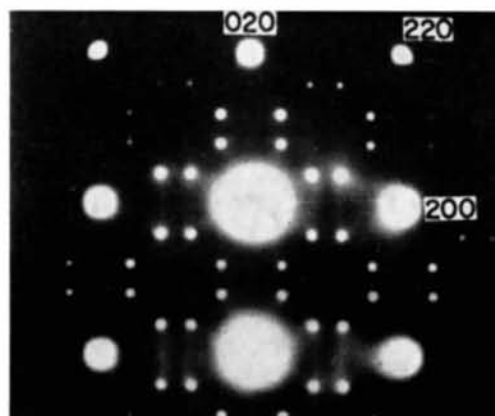


Fig. 2. (001) diffraction pattern of ordered  $\text{TiO}_{1.25}$ .

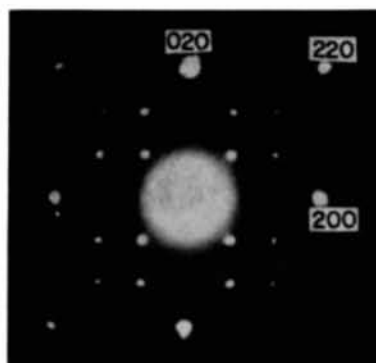
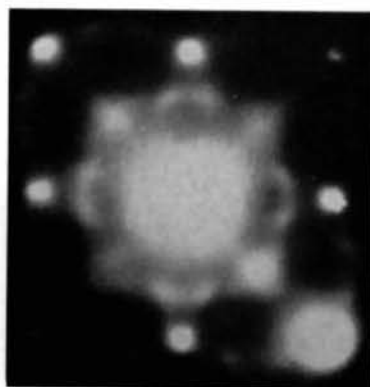
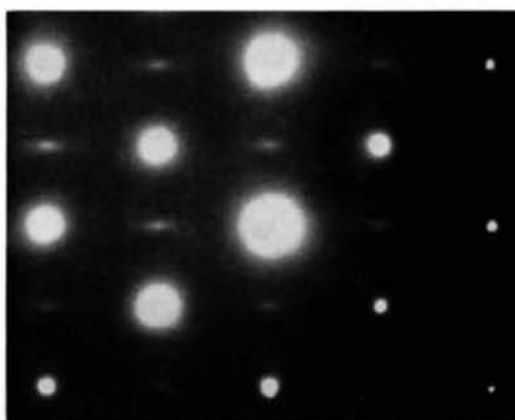


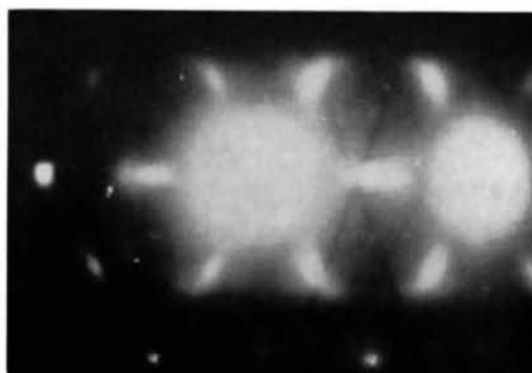
Fig. 3. (001) diffraction pattern of the 'transition' structure.



(a)

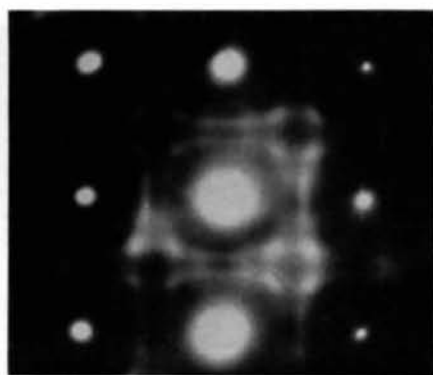


(b)



(c)

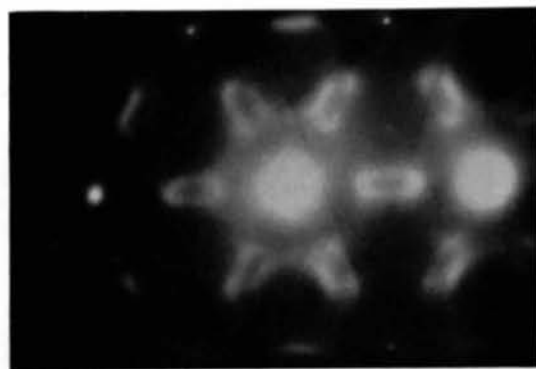
Fig. 4. Diffraction patterns of disordered  $\text{TiO}_{1.0}$ . (a) (001) orientation, (b) (110) orientation, (c) (111) orientation.



(a)

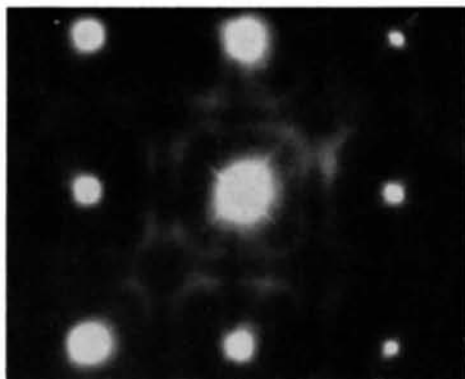


(b)



(c)

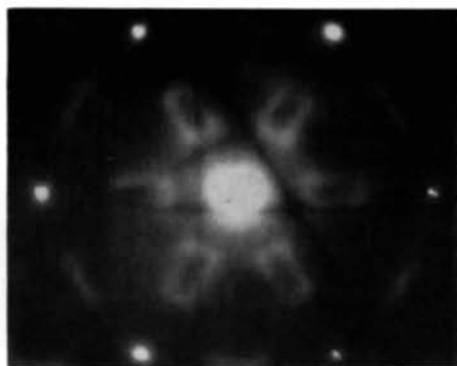
Fig. 5. Diffraction patterns of disordered  $\text{TiO}_{1.19}$ . (a) (001) orientation, (b) (110) orientation, (c) (111) orientation.



(a)



(b)



(c)

Fig. 6. Diffraction patterns of disordered  $\text{TiO}_{1.25}$ . (a) (001) orientation, (b) (110) orientation, (c) (111) orientation.

Table 1. *The changes in the lengths of the vectors 1, 2 and 3 shown in Fig. 7, as a function of composition*

Composition ( $x$ in $\text{TiO}_x$ )	Vector 1	Vector 2	Vector 3
1.00	0.50	0.45	
1.05	0.47		0.53
1.09	0.45		0.51
1.19	0.43		0.51
1.25	0.41		0.50

### The relation of diffuse scattering to the Fermi surface

The sharpness of the diffuse features in the electron diffraction patterns illustrated indicates that the range of correlation in the positions of the vacancies is of the order of 50 to 100 Å. This suggests that if, as is usual in considerations of atomic ordering, the energy of the system is described in terms of the sum of interactions between pairs of atoms, then the interatomic interactions in TiO must contain long-range components of considerable importance.

In the various theoretical treatments of binary  $AB$  alloys, the pair interaction potential of interest is  $V(\mathbf{r}) = \frac{1}{2}\{V^{AA}(\mathbf{r}) + V^{BB}(\mathbf{r}) - 2V^{AB}(\mathbf{r})\}$  where  $V^{AA}(\mathbf{r})$  is the interaction between two  $A$  atoms separated by the vector  $\mathbf{r}$ , and so on. To deal with the ordering of vacancies of Ti and O in a TiO lattice, the number of ordering entities is greater than two and several such energy terms must be postulated, with a corresponding increase in the complication of the theoretical treatment of the ordering process. However, since we are not attempting here a quantitative account of the degree of ordering, but are considering only the form of the interatomic interaction function and the qualitative aspect of the diffuse scattering array, it will be sufficient to work on the assumption that the simpler situation appropriate to binary alloys gives a reasonable approximation to the essential points in the behaviour of the system.

The fact that TiO is metallic with a high electronic conductivity suggests that the source of the long-range interatomic interaction may be the electronic energy term which has recently been shown to be important for the ordering of alloys. In the case of ordered superlattices it has been shown by Sato & Toth (1961) that the periodicities of long-period antiphase domain superlattices, and the variation of these periodicities with electron/atom ratio, may be explained by the requirement that a Brillouin zone boundary should be introduced at, or just inside, the Fermi surface in order to reduce the energy of the conduction electrons. In a more detailed analysis of this concept, Tachiki & Teramoto (1966) emphasized the importance of nearly flat areas of the Fermi surface, which make the most important contributions to this energy term.

A possible formulation in terms of an interatomic energy term, required for considerations of short-range order, is suggested by the results of a consideration of the perturbations of electron density due to a point

defect in a metal by Friedel (1954) and others. However it is not necessary to consider the case of a disordered alloy as an extrapolation of the case of a single point defect. This was shown by Krivoglaz & T'u Hao (1969) who pointed out that, to second order in perturbation theory, the part of the conduction electron energy of an alloy depending on the state of order could be effectively expressed as a long-range interaction potential in a pairwise Hamiltonian. The electronic contribution to  $V(\mathbf{r})$  is long-range and oscillatory, corresponding to a discontinuity in  $V(\mathbf{k})$ , the Fourier transform of  $V(\mathbf{r})$ , at the Fermi surface. The form of the discontinuity depends on the curvature of the Fermi surface (Roth, Zeiger & Kaplan 1966; Krivoglaz, 1969). The spherical, free-electron surface gives no more than a logarithmic singularity in the derivative of  $V(\mathbf{k})$  at  $k=2k_F$  and the effect on  $V(\mathbf{k})$  is very small. A cylindrical portion of the Fermi surface gives a radical singularity in  $V(\mathbf{k})$ . A flat region gives a logarithmic singularity in  $V(\mathbf{k})$  for a  $\mathbf{k}$  vector which spans the distance between two flats, and therefore has the most profound effect on the effective two-atom interaction potential.

The relationship of  $V(\mathbf{k})$  with the short-range order in the system is given by solution of the ordering problem, which in its simplest form is equivalent to the solution of the three-dimensional Ising problem. Clapp & Moss (1966), using their simplified approximate solution in linear form, derived the relation

$$\alpha(\mathbf{k}) = \frac{C}{1 + 2m_A m_B \beta V(\mathbf{k})}$$

where

$\beta = 1/KT$ ;  $K$  is Boltzmann's constant, and  $T$  temperature;

$C$  is a constant;

$m_A$  and  $m_B$  are the fractions of  $A$  and  $B$  atoms present in the alloy  $AB$ .

$\alpha(\mathbf{k})$  is given by summing the Fourier series with the order parameters  $\alpha(\mathbf{r}_{ij})$  as coefficients and so is proportional to the diffuse scattering intensity. This suggests that maxima of diffuse scattering intensity will occur at  $\mathbf{k}$  values corresponding to minima of  $V(\mathbf{k})$ . In other approximate solutions, the constant  $C$  is replaced by a function of  $\mathbf{k}$ , but the correlation of a maximum in  $\alpha(\mathbf{k})$  with a minimum in  $V(\mathbf{k})$  remains. Hence one would expect that the maxima of diffuse scattering for a disordered alloy should correspond to the minima in  $V(\mathbf{k})$  associated with  $\mathbf{k}$  vectors joining flat regions of the Fermi surface.

The approximate solutions of the ordering problem may be considered accurate only for temperatures well above the critical temperature for ordering  $T_c$ . However, because the correlation of scattering intensity with the flat areas of the Fermi surface applies both for this case and for considerations of ordered superlattices for temperatures below  $T_c$ , it is reasonable to suppose that it might apply for temperatures just above  $T_c$ , as in the present case.



Moss (1969) has recently shown that for the case of copper-gold alloys there is an excellent correlation between the most recent determinations of the shape of the Fermi surface with the observed configuration of diffuse scattering given by the disordered alloys just above the critical temperature. Therefore it may be expected that a similar correlation might be found in the case of TiO, for it is reasonable to suppose that the long-range part of the vacancy interaction has the same sort of dependence on the Fermi surface as the interatomic interaction in Cu-Au. The TiO case is more complicated since there are more ordering entities and interactions to be considered than in the case of binary alloys. However, a recent statistical mechanical analysis on TiO vacancy ordering, similar to the Clapp-Moss analysis, has shown a similar connexion between the order parameters and  $V(\mathbf{k})$  (Shirley, 1970).

The Fermi surface of TiO, which we will relate to the diffuse scattering, is that for the average NaCl-type lattice. In treating the problem from the point of view of short-range order theory, we make a considerable approximation since, as we have shown, the range of ordering in the 'disordered' state may be as great as 100 Å. However, if we assumed ordered superlattices to exist over such distances and treated the problem in terms of fitting Brillouin zone boundaries, diffuse because of the small effective crystal size, to flat portions of the Fermi surface, the same considerations would apply and the results would be the same.

#### Comparisons with the Fermi surface for TiO

The band structure of TiO has been calculated by Ern & Switendick (1965) using the augmented plane-wave method (APW), but assumed a TiO lattice with no vacancies. Hence in addition to the normal limitations of the APW method the calculations may be in error owing to omitting from consideration the 16.7% vacancies. The calculation of Schoen & Denker (1969) used the virtual crystal approximation to allow for the presence of vacancies but did not give any Fermi surface data and so Ern & Switendick's results are used here.

Ern & Switendick assumed the crystal to be composed of  $\text{Ti}^+$  ('valency' electrons  $3d^24s^1$ ) and  $\text{O}^-$  ( $2s^22p^5$ ). The Ti  $3d-4s$  band is incompletely filled and there is a considerable gap between this and the filled oxygen  $2p$  band. It seems reasonable to assume that the introduction of an oxygen vacancy removes at the same time 5 electrons and 5 states from the  $2p$  band which therefore remains full. The introduction of a Ti vacancy removes the one Ti electron and one state from the  $2p$  band but also removes two electrons from the  $3d-4s$  band. Then the number of nearly-free electrons in the  $3d-4s$  band depends on the concentration of Ti vacancies only. For example, with no vacancies in  $\text{TiO}_{1.0}$  the  $3d-4s$  band has 2 electrons per TiO pair while  $\text{TiO}_{1.0}$  with 15% Ti vacancies contains  $2 \times 0.85 = 1.70$  electrons and  $\text{TiO}_{1.25}$ , with 22% Ti vacancies

contains  $2 \times 0.78 = 1.56$  electrons. Thus a progressive decrease in the number of electrons in the band is expected with increasing oxygen concentration in the samples.

The Fermi surface for non-defective TiO as calculated by Ern & Switendick is illustrated in Fig. 8. The various bands shown are the overlapping sub-bands, each containing 2 electrons when filled. The filled portions of each are shaded. Although the effect of vacancies is not known in detail, one would expect a decrease in the shaded areas. However, in order to obtain agreement with the observed diffuse scattering in the electron diffraction patterns, we must postulate that the limit of the filled region is as indicated by the dotted lines. This represents an increase in two and a decrease in one of the filled regions, suggesting that for the  $\text{TiO}_{1.0}$  with no vacancies the filled regions should be even more extensive. As well as a shift of the boundaries, we have also postulated some changes of curvature to produce flatter regions, as seems reasonable.

The justification for assuming that the dotted lines of Fig. 8 represent the Fermi surface for  $\text{TiO}_{1.0}$  lies in the agreement with the observations on diffuse scattering for that composition and also with the explanation it offers for the progressive change in form of the

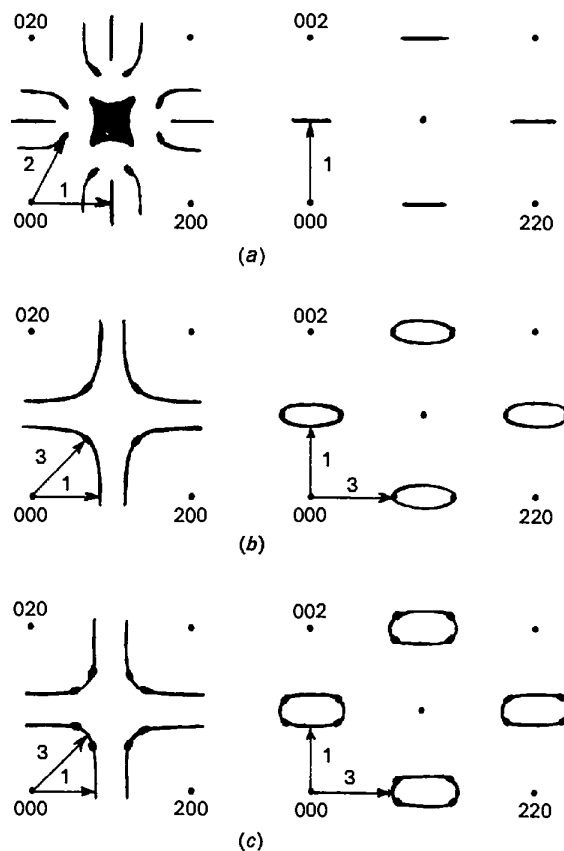


Fig. 7. Sketches of the diffuse scattering from disordered (a)  $\text{TiO}_{1.0}$ , (b)  $\text{TiO}_{1.19}$  and (c)  $\text{TiO}_{1.25}$ .

diffuse scattering as the composition is changed. The correlation of vectors between flat, or nearly flat, regions of the Fermi surface and the vectors from reciprocal-lattice points of the fundamental lattice to diffuse maxima is shown by equating numbered vectors in Fig. 8 with vectors drawn on sketches of the various diffraction patterns in Fig. 7.

For the  $\text{TiO}_{1.0}$  composition, the vector **1** in band 2 is correlated with the vector **1** from 000 to 100 in the (001) and (110) patterns and also gives the diffuse disc at the 110 position which bisects the line from the 111 and  $1\bar{1}\bar{1}$  reciprocal-lattice points. The vector **2** occurring in band 3 is in the [120] reciprocal-lattice direction and gives rise to the diffuse maxima around the 100 position as shown in the (001) pattern.

As the oxygen content increases, it is postulated that the vector **2** in band 3 ceases to be effective, and the vector **3** in band 1, extending in the [110] direction between flat areas, becomes important. This vector gives rise to the strong diffuse maxima along the line from 000 to 220 as indicated in the sketches for (001) patterns of  $\text{TiO}_{1.19}$  and  $\text{TiO}_{1.25}$ . As the titanium vacancy concentration increases, the length of the vector **3** decreases slightly as indicated in Table 1. For  $\text{TiO}_{1.25}$  the strength of the spots has decreased, presumably because the areas of the Fermi surface joined by vector **3** have become more curved.

The prominent pairs of streaks corresponding to the intersection of the Ewald sphere with the twin parallel discs of diffuse scattering about the 100 position are attributed to the vector **1** which decreases in length steadily with the number of titanium vacancies, as the number of electrons in band 2 is reduced and the shaded area of band 2 shrinks. This gives the effect that the oval-shaped loops of diffuse scattering seen in

the (110) and (111) patterns become fatter with increasing oxygen content.

From a detailed study of the form of the bands given by Ern & Switendick (1965) it is clear that the variation of the Fermi surface position, indicated by the change in diffuse scattering as the composition is changed from  $\text{TiO}_{1.0}$  to  $\text{TiO}_{1.25}$ , is of approximately the right magnitude to correspond to a variation of the number of electrons per atom pair from 1.70 to 1.56, as expected. Also, the observation that the vector **3** changes more slowly than vector **1** with composition is consistent with the relative slopes of the theoretical curves of band energy *vs.* distance along the appropriate lines in *k* space.

Thus it appears that the idea that the Fermi surface is imaged in the diffuse scattering from disordered TiO is a reasonable one. Admittedly, the agreement with the calculated band structure is not exact, but the modifications to the theoretical picture which must be made are probably no greater than the uncertainties which may arise from the necessary approximations made in order to render the calculations feasible.

### Discussion

The correlation between the diffuse scattering intensity distribution and the form of the Fermi surface for disordered TiO appears to be sufficiently good to suggest that the relationship is a real one. The fact that in the case of disordered alloys, for which a much more accurate picture of the Fermi surface is available, this correlation has been shown to be detailed and accurate (Moss, 1969) suggests that the form of the diffuse scattering may be used as a useful check on the accuracy of the theoretical Fermi surface where this is known

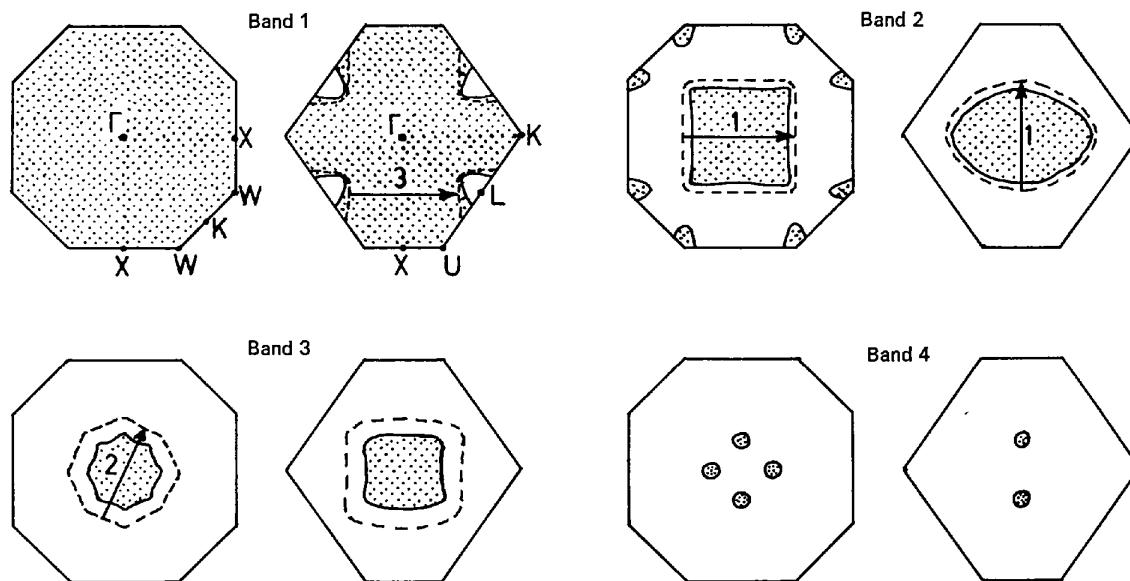


Fig. 8. The Fermi surface of non-defective TiO calculated by Ern & Switendick (1965) with the suggested changes indicated by the dotted lines.

with less precision, as in the case of TiO. It therefore appears that by this means useful information may be obtained for the study of Fermi surfaces, and hence the electronic properties, of any disordered material having a high concentration of defects.

While the present study has been made by electron diffraction, the relation between the diffuse scattering and the electronic energy term holds for any diffraction process which is reasonably close to kinematical. The same correlations could be observed for diffraction of X-rays or neutrons if suitable single crystal specimens are available. Electron diffraction offers the advantage of much greater ease in obtaining, observing and interpreting single-crystal patterns. The well-known occurrence of strong dynamical effects in electron diffraction patterns can result in perturbations of the diffuse scattering as, for example, by the Kikuchi lines visible in several of the diffraction patterns. However, it has been argued by Cowley (1965) and shown quantitatively by the detailed calculations of Fisher (1969) that in the case of diffuse scattering from vacancies or substitutional disorder the dynamical effects result only in multiplication of the kinematical intensities by a monotonically varying function which does not distort the detailed configuration of the diffuse scattering. Discrepancies in the intensities of corresponding points on diffraction patterns of different orientations can be noticed – for example, at the 100 position in Fig. 4(a) and (b) as discussed previously. These may be due to dynamical diffraction effects but it is also possible that the intensity differences reflect that the diffraction patterns were obtained from different specimens (cut from the same material) which could have been subject to slightly different quenching rates. Since it is the geometrical distribution of the diffuse scattering that is of interest here, these discrepancies are of little concern.

It is interesting to speculate that the variation of the form of the Fermi surface which we have deduced from the diffuse scattering configuration for TiO may have some bearing on the variation of various electrical properties of the material. For example, it appears that for  $\text{TiO}_{1.0}$  we must make use of vector 2 in band 3, rather than vector 3 in band 1 which is involved for higher oxygen concentrations. This implies that a change in the portions of the Fermi surface which are important in this respect, and possibly for other interactions of electrons with the lattice, takes place at around 50% oxygen. It has been observed, in fact, by Banus & Reed (1969) that there was a change in sign of the temperature coefficient of resistivity of TiO as the composition changed from  $\text{TiO}_{1.0}$  to oxygen-rich compositions. Also, the Seebeck coefficient changes sign and the graph of susceptibility *vs.* composition changes slope at the  $\text{TiO}_{1.0}$  composition.

From the structural point of view, the observations of the diffuse scattering are of interest in shedding considerable light on the nature of the disordered state for TiO and on the transition from short-range to long-

range order. In general there is little correlation between the positions of the diffuse maxima for the high temperature phase and the positions of the sharp spots from the ordered superlattices. This suggests that the electronic energy terms are largely responsible for the configurations of diffuse scattering whereas the requirements of a periodic structure with reasonable-size unit cells limit the possible positions for the sharp spots.

Partial exceptions, showing some correlation between sharp and diffuse spot positions, occur for the limiting compositions  $\text{TiO}_{1.0}$  and  $\text{TiO}_{1.25}$  which, significantly, correspond to the two compositions having fully ordered superlattices at low temperatures. For  $\text{TiO}_{1.0}$  the four diffuse spots around the 100 positions in Fig. 4(a) are close to the four corresponding sharp spots of Fig. 1. For  $\text{TiO}_{1.25}$  the four sharp spots around 100 in Fig. 2 lie close to the two diffuse streaks about 100 for the disordered material [Fig. 6(a)]. In fact, weak diffuse lines may be seen joining the spots of Fig. 2 forming part of the same configuration as in Fig. 6(a).

The correlation between the minima of  $V(\mathbf{k})$ , indicated by diffuse scattering maxima, and the likely positions for sharp superlattice reflexions has been emphasized for the case of alloys by Clapp & Moss (1968). The implication is that the long-range electronic interactions will tend to determine the form of the superlattice by providing minima of  $V(\mathbf{k})$  but the superlattice structure is limited by considerations of the basic symmetry and detailed interatomic configurations determined by the strong short-range interactions.

In this respect the observation of the transition structure as an intermediate stage between ordered and disordered TiO over a large range of composition is interesting. Here ordering has taken place only to the extent of restricting the vacancies to every third (110) atomic plane. The four resulting spots about the 110 position in Fig. 3 are close to, but not coincident with, the four diffuse spots in this configuration which appear strongly for all compositions of the disordered material except for the limiting cases of  $\text{TiO}_{1.0}$  and  $\text{TiO}_{1.25}$ . Hence it appears that ordering takes place first in such a way that the superlattice spots come as close as possible to the most important minima of  $V(\mathbf{k})$ .

It is notable, however, that the four spots about 110 are not minima of  $V(\mathbf{k})$  for  $\text{TiO}_{1.0}$ . In this case there is a strong minimum at the 110 position itself, but there are also minima at the four positions about 100 at the ends of the diffuse arcs [Fig. 4(a)]. Upon ordering, superlattice spots occur at these latter four positions and, because of the requirement that the reciprocal lattices of ordered structures be periodic, superlattice spots occur also at the four corresponding positions about 110 (*i.e.* where the transition structure spots lie) despite the fact that these positions are not  $V(\mathbf{k})$  minima. (See the ordered  $\text{TiO}_{1.0}$  (001) pattern, Fig. 1.)

All these considerations re-emphasize the general principle that to obtain empirical information on pairwise interactions between atoms in crystals the most

informative approach is the study of diffuse scattering from disordered material. Information from ordered states is less informative because the requirements of the periodic structure limit the possible atomic arrangements.

The authors gratefully acknowledge many stimulating and helpful discussions with Professor S. Moss of M.I.T. Further information concerning the theoretical Fermi surface of TiO was kindly supplied by Dr V. Ern. We appreciate the assistance given in specimen preparation by Dr A. Jostsons and Mr J. Napier of the Australian Atomic Energy Research Establishment, Dr D. Robertson and Mr C. Roberts of the Metallurgy Department, University of New South Wales and Dr D. Michele of the Tribophysics Division, CSIRO. This work was supported by a grant from the Australian Atomic Energy Commission. One of us (JRC) acknowledges the support of a Commonwealth Postgraduate Award.

### References

- BANUS, M. D. & REED, T. B. (1969). *Proceedings of Second Solid State Chemistry Conference. Chemistry of Extended Defects in Non-metallic Solids*. Scottsdale, Arizona.
- CLAPP, P. C. & MOSS, S. C. (1966). *Phys. Rev.* **142**, 418.
- CLAPP, P. C. & MOSS, S. C. (1968). *Phys. Rev.* **171**, 754.
- COWLEY, J. M. (1965). *International Conference on Electron Diffraction and Crystal Defects*, J-5. Australian Academy of Science.
- COWLEY, J. M. (1969). *Proceedings of Second Solid State Chemistry Conference. Chemistry of Extended Defects in Non-metallic Solids*. Scottsdale, Arizona.
- ERN, V. & SWITENDICK, A. C. (1965). *Phys. Rev.* **137A**, 1927.
- FISHER, P. M. J. (1969). Ph. D. thesis, Univ. of Melbourne.
- FRIEDEL, J. (1954). *Advanc. Phys.* **3**, 446.
- HILTI, E. (1968). *Naturwissenschaften*, **55**, 130.
- KRIVOGLAZ, M. A. (1969). *Theory of X-ray and Thermal Neutron Scattering by Real Crystals*. New York: Plenum Press.
- KRIVOGLAZ, M. A. & T'U HAO (1969). *Collection Defects and Properties of the Crystal Lattice*. Kiev: Izd. 'Naukova Dumka'.
- MOSS, S. C. (1966). *Local Atomic Arrangements Studied by X-ray Diffraction*. Edited by J. B. COHEN & J. E. HILLIARD. p. 100. New York: Gordon & Breach.
- MOSS, S. C. (1969). *Phys. Rev. Letters*, **22**, 1108.
- ROTH, L. M., ZEIGER, A. J. & KAPLAN, T. A. (1966). *Phys. Rev.* **149**, 519.
- SATO, H. & TOTH, R. S. (1961). *Phys. Rev.* **124**, 1833.
- SCHOEN, J. M. & DENKER, S. P. (1969). *Phys. Rev.* **184**, 864.
- SHIRLEY, C. G. (1970). M. Sc. Thesis, Univ. of Melbourne.
- TACHIKI, M. & TERAMOTO, K. (1966). *J. Phys. Chem. Solids*, **27**, 335.
- WATANABE, D. (1965). *International Conference on Electron Diffraction and Crystal Defects*, Australian Academy of Science. I-C-3.
- WATANABE, D., CASTLES, J. R., JOSTSONS, A. & MALIN, A. S. (1967). *Acta Cryst.* **23**, 307.
- WATANABE, D., TERASAKI, O., JOSTSONS, A. & CASTLES, J. R. (1968). *J. Phys. Soc. Japan*, **25**, 292.
- WATANABE, D., TERASAKI, O., JOSTSONS, A. & CASTLES, J. R. (1969). *Proceedings of Second Solid State Chemistry Conference. Chemistry of Extended Defects in Non-metallic Solids*. Scottsdale, Arizona.

*Acta Cryst.* (1971). A **27**, 383

## Rigid-Body Motion in Phosphorus Chalcogenides

BY R. A. FORDER

*University Chemical Laboratories, Lensfield Road, Cambridge*

(Received 18 December 1970)

The thermal parameters of  $P_4S_5$ ,  $P_4S_7$ ,  $P_4S_{10}$  and  $P_4Se_5$  have been analysed on the basis of the rigid-body hypothesis, using both Cruickshank's and Shomaker & Trueblood's methods. For these compounds, at least with the data at present available, the fit to the rigid-body model is only moderate, and there is no significant difference in the results of the two methods. Librational corrections to bond lengths have been calculated.

### Introduction

Considerable interest has been shown over the last few years in analysing the thermal motion of molecules in crystals on the assumption that they are, to a reasonable approximation, moving as rigid bodies.

In his original paper, Cruickshank (1956) attempted to describe this motion in terms of two symmetric

tensors,  $T$  and  $\omega$ , representing the mean-square translational vibrations of the mass centre and the mean-square angular oscillations (librations) respectively. The chief problem here is the choice of the centre of libration when this is not determined by symmetry, though in many cases a reasonable approximation may be the centre of mass.

Pawley (1963) and others attempted to solve this