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An Electron Microscope Study of Some Titanium Sulphides

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Crystals of titanium sulphides of nominal composition $Ti_{1.25}S_2$ (Ti_5S_8), $Ti_{1.50}S_2$ (Ti_3S_4), and $Ti_{1.60}S_2$ (Ti_4S_5) have been prepared and studied by transmission electron microscopy. Lattice fringe resolution has shown faulting to be commonplace in the $Ti_{1.25}S_2$ and $Ti_{1.50}S_2$ compositions, but infrequent in the $Ti_{1.60}S_2$ material. In all crystals, repeat distances between lattice fringes have been found which do not correspond to previously reported titanium sulphides and are considered to arise from new structures. Diffraction evidence supports this view. Although it is likely that the existence of these new structures is due to different titanium to sulphur stoichiometries, the possibility that they are polytypes or due to impurities is also considered.

Introduction

Over the course of the last few years, careful X-ray studies and more especially electron microscope studies, have shown that a number of oxide phases previously thought to have broad composition ranges are made up of a large number of structurally related compounds with exact stoichiometries (*1*, *2*). Much of this information has come from use of the technique of lattice imaging, whereby unit cells of the material under consideration are imaged in one or two dimensions (*3*). This takes place regardless of local disorder in the crystal, and hence structural information about highly disordered and poorly ordered phases is available at a unit-cell level. In this way, a vast amount of structural information is made available that is inaccessible to X-ray diffraction techniques, because with this latter technique, average information from relatively large volumes of sample are obtained.

In view of the significance of such studies in understanding the chemistry of nonstoichiometric oxides, it would appear profitable to examine other nonstoichiometric systems by electron microscopy. One group of compounds which exhibit stoichiometry ranges and for which the presence of ordered intermediate phases has been confirmed are the transition metal sulphides (*4*, *5*). In general, these compounds, which are formed by the metals V, Cr, Fe, Co, and Ni, can be considered to be derived from a nickel arsenide (B8) parent. The anions are in hexagonal close packing, and one phase differs from the next in the number of vacant metal sites present in the unit cell. The unoccupied sites are limited to every other layer of metal atoms in a direction perpendicular to the close-packed anion layers, and are also ordered within each layer. The limiting case occurs when every other cation layer is totally unoccupied. The structure is then of the CdI_2(C6) type. The structural geometry of this transition has been well documented (*6*, *7*).

As would be expected, the sulphides of titanium in the phase interval TiS to TiS_2 are similar to those of the other 3d transition metals mentioned above. However, they differ from them in two ways; the vacancies in the defective cation layers are distributed at random, and the sulphur packing in the intermediate phases between TiS and TiS_2 is complex and varies from one material to the next (*5*). Because of this, the titanium sulphides were considered to be of greater interest, and were chosen for preliminary study.

The present study aimed at surveying the structures of the titanium sulphide phases in the composition interval TiS to TiS_2 by electron microscopy. In the first instance, those with large unit cells, Ti_5S_8, Ti_3S_4, and Ti_4S_5, were selected and lattice-fringe resolution used to study structural disorder. The results of this study are presented here. Each compound showed structural complexity, and a number of previously unreported phases were found. These results are discussed in terms of nonstoichiometry but the possibility of polytypism occurring in these materials is also considered.

Structural Relationships Between the Titanium Sulphides

Structural information for the compounds reported in the phase range TiS to TiS_2 is given in Table I. The structures of the end members of the series TiS and TiS_2 are shown in Fig. 1. As stated above, TiS has the nickel arsenide structure, and TiS_2 the cadmium iodide structure. The transition from TiS_2 to TiS can be envisaged as a gradual filling of the empty layers of octahedral sites in the C6 structure. Intermediate compositions can thus be conveniently represented by the formula $Ti_{1+x}S_2$; the fraction of occupied sites in the partly filled layers then being given by x. This filling takes place in a random fashion, and each intermediate structure appears to have a homogeneity range associated with a variable degree of partial filling of the available sites. Table I contains the degree of occupancy of the cation sites in the intermediate structures and the homogeneity range where known. Many authors have used Daltonide formulae Ti_mS_n to represent these phases, and these are also included in the table, although due to the homogeneity ranges present this nomenclature has sometimes led to confusion.

The hexagonal close packing of the anion layers found in TiS and TiS_2 does not persist over the whole of the stoichiometry range. Instead, complex sequences of stacking are found for the intermediate structures, each of which appears to be associated with a definite titanium to sulphur ratio as shown in Table I. An attempt to rationalize the sulphur stacking sequences of the compounds in the composition range TiS to Ti_2S_3 has been made by Wiegers and Jellinek (*13*). The fractional occupancies of the cation layers can be plotted against distance parallel to the hexagonal c parameter to give a series of "occupation waves." Wiegers and Jellinek point out that the sulphur layers corresponding to troughs in these waves are in cubic (c) arrangement while those near crests are in hexagonal (h) arrangement. However, this suggestion does not hold good for the phases Ti_2S_3, Ti_5S_8, and TiS_2 or the polytypes reported by Tronc and Huber (10), and the reason why such complex sulphur layer-stacking sequences occur in the titanium sulphides must still be regarded as uncertain.

Experimental

Samples of overall composition $Ti_{1.25}S_2$ (Ti_5S_8), $Ti_{1.50}S_2$ (Ti_3S_4), and $Ti_{1.60}S_2$ (Ti_4S_5) were prepared by heating titanium sponge and sulphur crystals in silica tubes sealed under a pressure of less than 1×10^{-4} Torr. The purities of the starting materials, quoted by the supplier, B.D.H. Limited, were 99.89% for the titanium and better than 99.9% for the sulphur. The principal impurities in the titanium are oxygen

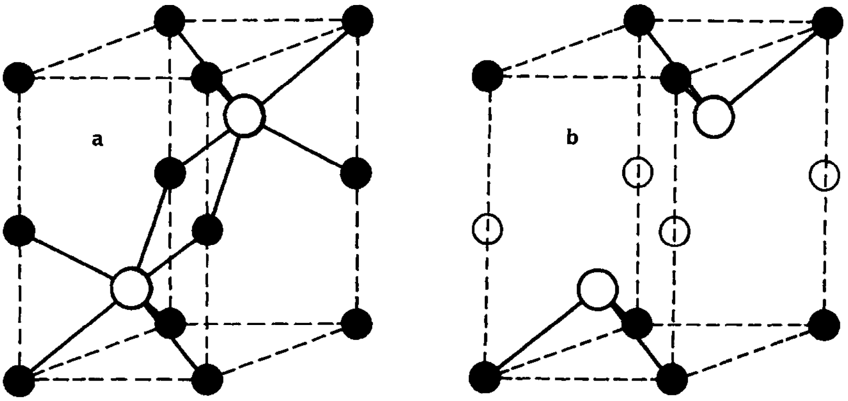

FIG. 1. A comparison of (a) the TiS and (b) the TiS_2 structures. Sulphur atoms are represented by large open circles and titanium atoms by filled circles. The vacant octahedral sites in TiS_2 represented by small open circles are partially filled in the intermediate phases.

TABLE 1

THE STRUCTURES OF TITANIUM SULPHIDES IN THE COMPOSITION RANGE TiS TO TiS_2

Nominal composition	Phase	Symmetry	Unit cell dimensions (nm) (a)	(c)	Number of sulphur layers per unit cell	Sulphur packing	Occupancy of metal sites	Homogeneity range at 1000°C
TiS_2	TiS_2	trigonal, $P\bar{3}ml$	0.3408	0.56912(8)	2	$(h)_2$	h 1.0 h 0.05(8)	$Ti_{1.04}S_2$–$Ti_{1.105}S_2$(8)
$Ti_{1.25}S_2$	Ti_8S_{12}	hexagonal, —	0.343	3.43(8)	12	—	—	$Ti_{1.325}S_2$–$Ti_{1.34}S_2$(8)
	Ti_5S_8	rhombohedral, $R\bar{3}m$	0.3418	3.436(9)	12	$(cchh)_3$	c 1.0 c 0.2 h 1.0 h 0.2(9)	—
	Ti_8S_{12}	hexagonal, $P6_3mc$	0.342	3.438(10)	12	$(cchhch)_2$	c 1.0 c 0.25 h 1.0 h 0.25 c 1.0 h 0.25(10)	—
$Ti_{1.33}S_2$	Ti_2S_3	hexagonal, $P6_3mc$	0.3426	1.1433(8)	4	$(ch)_2$	c 1.0 h 0.33 (8)	$Ti_{1.26}S_2$–$Ti_{1.45}S_2$(8)
	Ti_2S_3	hexagonal, $P6_3/mmc^a$	0.5936	2.2866(11)	8	$(ch)_4$	c 1.0 h 0.33 (11)	—
	$Ti_{2.45}S_4$	hexagonal, $P6_3mc$	0.34198	1.1444(12)	4	$(ch)_2$	c 1.0 h 0.227(12)	—
$Ti_{1.43}S_2$	Ti_2S_3	hexagonal, —	0.342	1.144(10)	4	—	—	—
			0.342	2.86(10)	10	—	—	—
			0.342	6.88(10)	24	—	—	—
			0.342	11.46(10)	40	—	—	—
$Ti_{1.50}S_2$	Ti_3S_4	rhombohedral, $R\bar{3}m$	0.3441	6.048(13, 14)	21	$(chchchh)_3$	c 0.95 h 0.7 c 0.7 h 0.95 c 0.5 h 1.0 h 0.5(13)	$Ti_{1.53}S_2$–$Ti_{1.56}S_2$(16)
$Ti_{1.60}S_2$	Ti_4S_5	hexagonal, $P6_3/mmc$	0.3439	2.893(13, 15)	10	$(chchh)_2$	c 0.9 h 0.9 c 0.6 h 1.0 h 0.6(13)	—
							c 0.875 h 0.875 c 0.65 h 1.0 h 0.65(15)	—
$Ti_{1.71}S_2$	Ti_8S_9	rhombohedral, $R\bar{3}m$	0.3425	2.6493(11)	9	$(chh)_3$	c 0.83 h 1.0 h 0.83(11)	$Ti_{1.67}S_2$–$Ti_{1.78}S_2$(16)
Ti_2S_2	TiS	hexagonal, $P6_3/mmc$	0.3299	0.6380(11)	2	$(h)_2$	h 1.0 h 1.0(11)	$Ti_{1.885}S_2$–$Ti_{2.03}S_2$(16)

[a] Pseudohexagonal. The true cell is monoclinic. Literature references are given in parentheses.

(500 ppm), iron (300 ppm) and water (100 ppm).

As the experiments were of a preliminary nature, these were considered adequate. For a similar reason, the reactants were not protected from the silica tube in any way. However, visual inspection of the silica tubes after heating, which was at 930°C, did not suggest that reaction between the silica and the sulphides had taken place to any great extent.

Tubes containing compositions $Ti_{1.50}S_2$ and $Ti_{1.60}S_2$ yielded plate-like crystals of up to 3 mm diameter after heating for a period of 88 days. Crystals of $Ti_{1.25}S_2$ were grown from microcrystalline material prepared by heating titanium and sulphur for 12 days at 930°C. This initial reaction product was resealed in silica as for the other samples, but a few milligrams of NH_4Cl was added as a mineralizing agent. The crystals grew over a period of 70 days.

Crystals of all three phases exhibited fracture rather than cleavage when crushed in an agate mortar. Electron microscope samples were prepared from this ground material; small crystallites being supported on carbon films in the conventional fashion. They were examined in an AEI EM6G electron microscope operating at 100 kV. Microdensitometer traces were obtained using a Joyce-Loebl microdensitometer.

Results and Interpretation

$Ti_{1.25}S_2$

Crystal fragments were sought which gave diffraction patterns containing the 00*l* reciprocal lattice row, as this is the only practical way of determining which of the Ti-S phases is present. Four different diffraction patterns were found, as shown in Fig. 2. The characteristic feature of all patterns is a set of bright subcell reflections, with a spacing of 0.573 nm, which did not vary from one pattern to another. The patterns differ from one another in the number of spots separating the subcell reflections. As seen in Fig. 2, this number is one, three, five, or seven. Continuous streaking, somewhat modulated into maxima, as expected from a series of planar faults (*17*), was also seen. The interplanar spacing values corresponding to the superlattice spots are 1.146 nm, 2.292 nm, 3.438 nm, and 4.584 nm.

The structural data listed in Table I show that the diffraction patterns of the phases Ti_2S_3, Ti_5S_8 (hexagonal and rhombohedral) and TiS_2 all contain a set of 00*l* reflections separated by approximately 0.57 nm. Between these, there will be one extra reflection for rhombohedral Ti_5S_8 and two for hexagonal Ti_5S_8, dividing the 0.57 nm spacing into equal parts. Neither the TiS_2 nor the Ti_2S_3 phase will show any extra reflections along the 00*l* row. Thus the diffraction pattern shown in Fig. 2(a) can be considered to arise from rhombohedral Ti_5S_8. The diffraction patterns shown in Figs. 2(b) and 2(d) cannot be equated to the diffraction patterns expected from any of the phases listed in Table I, and must arise from new structures in the system. In view of the pronounced 0.57 nm subcell, these new structures will show a resemblance to the phases in the Ti_5S_8-TiS_2 region of the phase diagram rather than those below Ti_2S_3 as the diffraction patterns of these latter materials do not show this marked periodicity.

The remaining pattern, shown in Fig. 2(c) cannot be assigned as easily. The intensities of the superlattice spots change rapidly as their

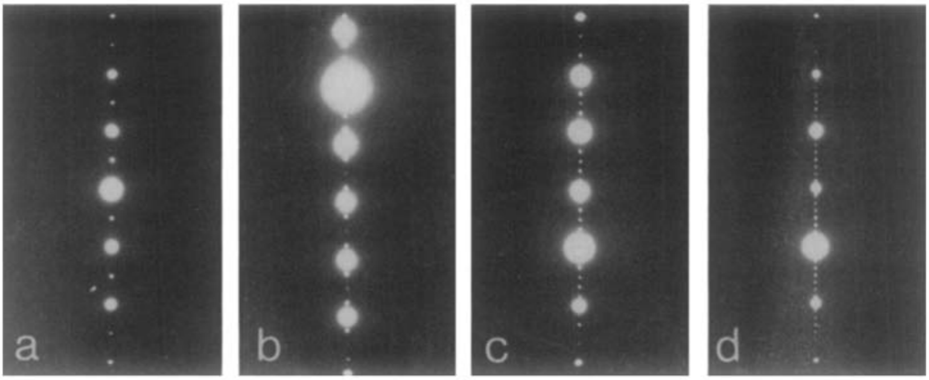

FIG. 2. Diffraction patterns from crystal fragments obtained from a sample of "Ti_5S_8." The vertical rows correspond to the 00*l* direction. (a) corresponds to rhombohedral Ti_5S_8 and (c) to hexagonal Ti_5S_8.

distance from the intense 000 spot increases, so that beyond the immediate neighbourhood of the central spot only two of the five superlattice spots remain visible. This effect is clearly visible in Fig. 2(c). Such a pattern would correspond to hexagonal Ti_5S_8, and this is considered to be the likely structure of the diffracting crystal. The reason for this doubling of the periodicity of the spot pattern close to the intense 000 reflection is uncertain. Double diffraction, which often causes the appearance of extra reflections in electron diffraction patterns, may be the reason, although a more constant distribution of intensity along the $00l$ row would be expected. The appearance of such forbidden reflections close to the central spot in MoO_3 crystals is frequently observed, and a similar process seems likely to be in operation here. Therefore, although there is some uncertainty present, the pattern shown in Fig. 2(c) is believed to arise from crystals of hexagonal Ti_5S_8.

The commonest crystal type met with in the electron microscope was the Ti_5S_8 phase. Lattice fringe images could be obtained from thin edges of the hexagonal phase when the c axis was normal to the electron beam. These always showed faulting; Fig. 3 being typical. The nature of the faults was always the same. The fringe separation across a fault [such as A or B in Fig. 3(a)] is exactly double the normal spacing of 3.44 nm. There is frequently a weak fringe between each wide pair, but not always so, possibly due to slight changes in focusing conditions (*3*). Microdensitometer traces across the fringes shown in Fig. 3 reveal that for faults A and B, the weak fringe is in the middle of the fault, while for fault C it is assymetrically placed. Taking the sulphur–sulphur distance as 0.2863 nm, and the unit cell of Ti_5S_8 as containing 12 sulphur layers, the central fringe in fault C divides the 6.88-nm unit into two parts, one of 11 sulphur layers and one of 13 layers.

These results show that coherent lamellae of different sulphur stackings are intergrown in the Ti_5S_8 phase. It is not possible to identify the nature of the material in these lamellae, except to note that they could be regions of rhombohedral Ti_5S_8, Ti_2S_3, or a new structure altogether.

A type of fault quite frequently found is shown in Fig. 3(c). In this, a black fringe drops in intensity for part of its length giving a short segment of a fault similar to the extended faults A and B, mentioned above. Microdensitometer traces across the region in Fig. 3(c) do not show any change in spacing within this faulted region. It is therefore possible that over this short segment of length 35 nm the stacking sequence of sulphur layers has altered, because of small regions of impurity, or because of local changes

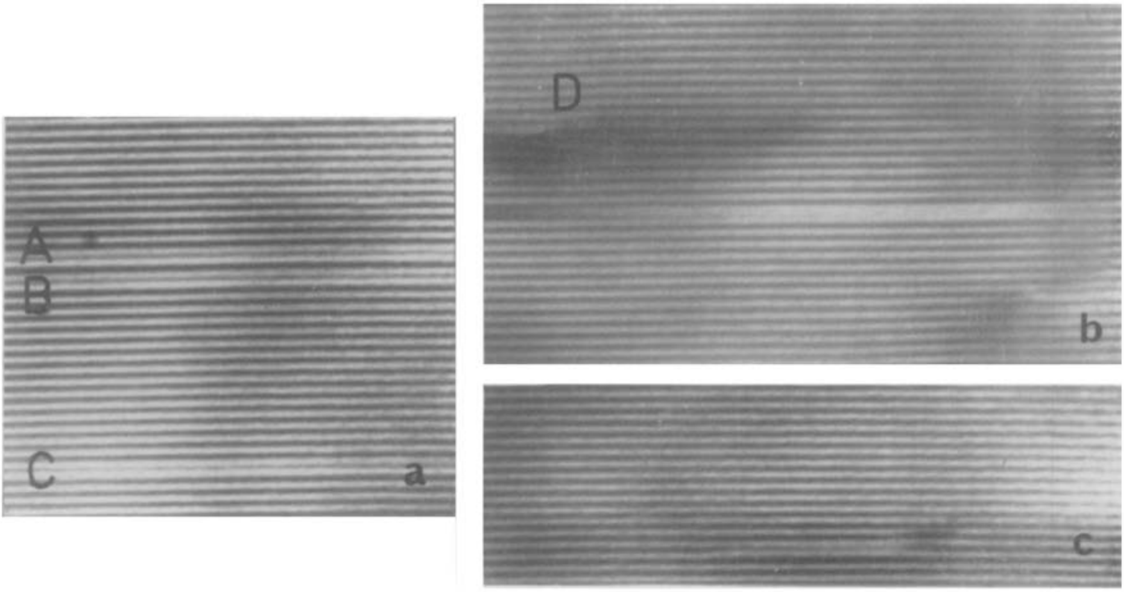

FIG. 3. Lattice fringe images of Ti_5S_8 showing faulting of the lattice. (See text for details). A pair of dislocations is indicated at D in (b). The separation of the undistorted fringes is 3.4 nm.

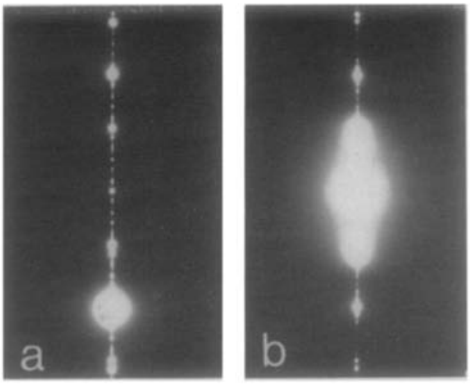

FIG. 4. Diffraction patterns from crystal fragments obtained from a sample of $Ti_{1.50}S_2$. The vertical rows correspond to the 00*l* direction.

in the titanium to sulphur ratio. A similar effect on a large scale is seen in the fault in Fig. 3(b).

$Ti_{1.5}S_2$

The c^* direction on diffraction patterns of all fragments studied was streaked more or less heavily from one sample to another as shown in Fig. 4. The streaking was modulated into maxima which were separated by approximately 0.57 nm on all patterns, though this subcell pattern was much less in evidence than in crystals from the $Ti_{1.25}S_2$ preparation. In addition, some diffraction patterns showed quite well-defined superlattice spots between the subcell spots. Two different arrangements of these spots were seen, one with 10 spots and one with 14 spots between every second subcell pair of maxima corresponding to spacings of 3.17 and 4.32 nm. These are shown in Figs. 4(a) and (b).

The data contained in Table I show that for each known structure, the spot spacing along 00*l* corresponds to the sulphur packing repeat unit along the hexagonal *c* direction, and not the *c* parameter itself. This repeat unit is $\frac{1}{2}c$ for crystals of hexagonal symmetry and $\frac{1}{3}c$ for crystals of rhombohedral symmetry referred to hexagonal axes. Clearly, in these crystals the degree of ordering present in the fragment of crystal can vary considerably, and the diffraction patterns above are representative of areas with (i) little order, (ii) a reasonably ordered phase with 11 sulphur layers per repeat unit, and (iii) a reasonably ordered phase with 15 sulphur layers per repeat unit, all in the *c* direction. These materials cannot be identified with any of the known structures listed in Table I and it is concluded that both these materials have new structures.

Lattice fringe images, as expected, showed very wide ranging disorder. Fig. 5 is typical. These images were formed by combining beams closest to the 000 spot with the undiffracted beam, and thus they will represent the repeat units along *c* and not the *c* unit-cell dimension unless diffraction effects similar to that found in the Ti_5S_8 crystals occur. In this case, the considerable streaking present does not allow an unequivocal decision to be made, and the lattice fringe separations must be interpreted as either being sulphur packing repeat units or unit-cell lengths.

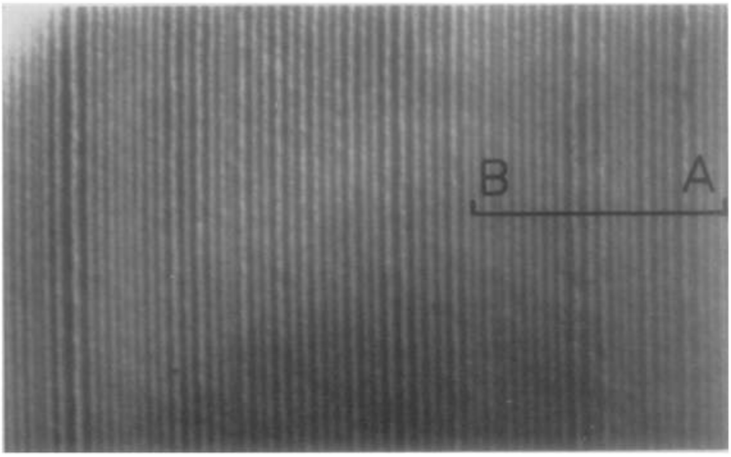

FIG. 5. Lattice fringe images of a crystal fragment obtained from a sample of $Ti_{1.50}S_2$. The fringe spacings vary from 2.3 nm to 4.6 nm.

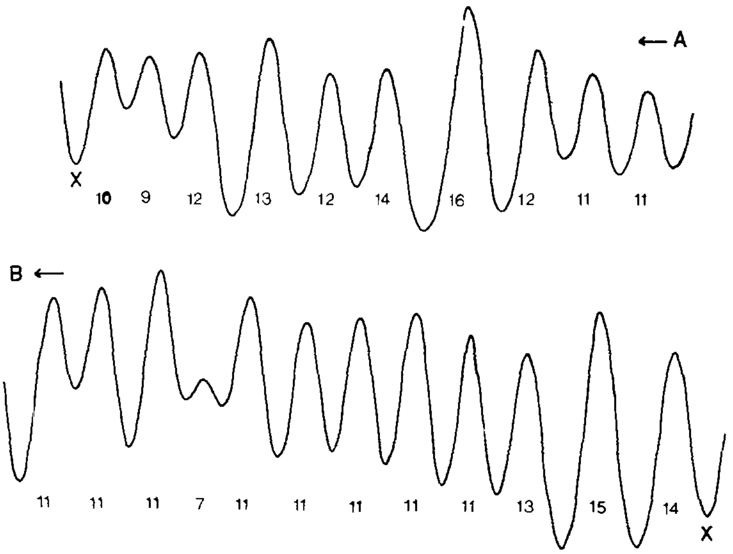

FIG. 6. Microdensitometer trace across the region AB in Fig. 5. The figures below each peak give the number of sulphur layers present between each of the dark fringes in Fig. 5 which correspond to the minima on the trace. The lower trace is continuous with the upper one, with the minima marked X duplicated above and below.

Microdensitometer traces across disordered regions showed that lattice fringes were always separated by integral numbers of sulphur layers, assuming a sulphur–sulphur distance of 0.288 nm, as is found in Ti_3S_4. A typical trace, with values ranging from 7 to 16 sulphur layers between fringes is shown in Fig. 6. A comparison with the data in Table I shows that many of the lamellae found in these crystals must represent new stacking types.

The literature value of the c parameter of Ti_3S_4 is 6.048 nm corresponding to 21 sulphur layers. Spacings of this size were not seen. However, as stated earlier, the rhombohedral symmetry of this phase means that only $00l$ reflections with $l = 3n$ are seen and the fringe spacing expected for Ti_3S_4 would be that corresponding to 7 sulphur layers. This smaller spacing was not noted either except as occasional lamellae. The conclusion to be drawn is that the Ti_3S_4 phase reported by Wiegers and Jellinek (*13*) was not present in the crystals studied in these experiments.

$Ti_{1.60}S_2$

These crystals, in contrast to the others studied, were almost perfectly ordered. A typical diffraction pattern and micrograph of lattice fringes are shown in Fig. 7. Unlike the previous crystals, the diffraction patterns of this material do not show an intensity variation suggestive of a subcell of approximately 0.57 nm. The spacing on the diffraction pattern is 2.023 nm which suggests that the phase has a repeat unit of 7 sulphur layers. This does not agree with the crystal data for Ti_4S_5 determined by Wiegers and Jellinek (*13*) but does fit with that expected for Ti_3S_4. Although the cell dimensions and symmetry cannot be found from the experimental data, is it reasonable to assume that the crystals are fairly well-ordered Ti_3S_4.

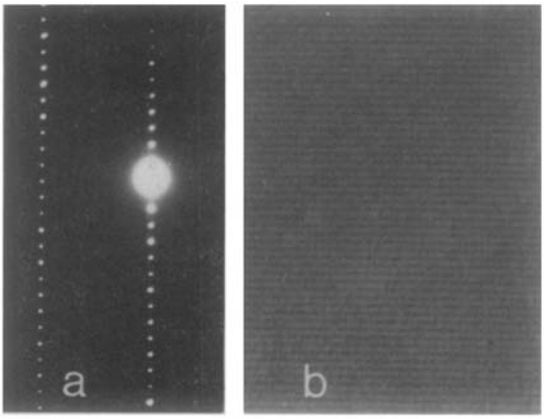

FIG. 7. (a) Diffraction pattern and (b) well-ordered lattice fringes of 2.02 nm spacing from a crystal fragment obtained from a sample of $Ti_{1.60}S_2$. In (a) the vertical rows correspond to the $00l$ direction.

Discussion

The examination of three apparently well-characterized phases in the titanium–sulphur system has revealed a degree of structural complexity previously unreported, although the study of Tronc and Huber (*10*) suggested that such complexity would be found. The results reported here are an extension of the studies of these latter authors on a finer scale, and confirm that a large number of structures exist in the phase interval designated as Ti_2S_3 by Jeannin (*8*). The fact that this complexity has not been reported previously is due to the limitations of the powder X-ray method, which has been the main technique used in determining the homogeneity ranges of the phases recorded in Table I. This limitation is pronounced when samples consist of very similar structure types with large unit cells, as seems to be the case here. One must conclude that X-ray powder photographs are not sensitive enough to distinguish the fine structural detail present in this region of the phase diagram.

Of the structures found, only two, Ti_5S_8 and Ti_3S_4, seem identical with those reported previously. All other materials are new structures in the sense that their diffraction patterns do not agree with the unit cell data of Table I. Although the present experimental evidence does not yield structural data, it does show that new stacking repeat units can occur. These new sequences could either be due to local composition changes or else due to polymorphism at fixed titanium-to-sulphur ratios. Both of these possibilities cannot be divorced from the mode of crystal growth, and this will be considered in the first instance.

The appearance of the crystals in each tube suggests that they grew from the vapour phase. They were found on the surface of the uncrystallized product, never within it, and were lightly attached to the bulk powder or to the tube walls. Each tube, when opened, released some H_2S, and this is likely to be the chemical transporting agent for the $Ti_{1.50}S_2$ and $Ti_{1.60}S_2$ compositions, and may well have been important in the growth of the $Ti_{1.25}S_2$ crystals, although ammonium chloride was deliberately added in this case to promote mineralization. Thus, composition variations are likely to be caused by changes in the rate of arrival of titanium and sulphur vapour species, at the growing $(00l)$ faces. This itself could be due to temperature variations during growth. As the total heating time was long, composition variations in the bulk would be expected to anneal out by way of titanium diffusion. However, the rearrangement of sulphur layers would be a more difficult process, and the sequence of stackings found could well be identical to those laid down during growth.

If the faulting found is due to composition variation, homogeneous samples of phases with other stackings should be readily prepared although careful control of the sulphur activity will be necessary. From the results obtained here, it would seem that phase regions close to Ti_5S_8 and Ti_3S_4 are promising, and in particular, the broad phase range quoted for Ti_2S_3 may yield new structures. This is supported by the findings of Tronc and Huber (*10*) who also prepared compositions within this phase range.

The stacking sequences observed may also arise from impurity concentrations in the growing crystal. Anderson, Brown, and Hutchison (*18*) have suggested that during growth crystals of niobium oxides doped with tin and fluorine reject these latter ions as impurities at the growing front until their concentration reaches a level at which they can nucleate a layer of another but similar structure type. This could apply to the fairly isolated faults seen in the $Ti_{1.25}S_2$ crystals, and more rarely in the $Ti_{1.60}S_2$ crystals, but would seem to be less applicable to the highly disordered $Ti_{1.50}S_2$ material. The small regions of fault shown in Fig. 3(c) are also more suggestive of regions containing impurities rather than composition fluctuations which would be expected to occur on a wider front.

The nature of the impurities is uncertain. The experimental conditions of preparation suggest that silicon may be a contaminant, although the sealed tubes used showed no sign of reaction or devitrification, and the product of such a reaction is likely to be a titanium silicide phase (*16*). A more likely impurity is oxygen. It is difficult to remove oxygen completely from powders, and in particular from the titanium sponge granules where the analysis showed it to be the major foreign element present. The presence of H_2S in the tubes after heating also suggests that the traces of water which were initially present could have also added oxygen to the solid lattice. The effect of small quantities of oxygen on the stacking of sulphur layers is unknown, but could be profound. In order to test this suggestion, an attempt is being made to prepare titanium oxysulphides with small known oxygen contents.

There is the possibility that the varying stacking sequences found are not new phases in the chemical sense of having differing sulphur-to-titanium ratios on going from one material to another, but are polytypes. Polytypism is common in layer lattices and has been found in these titanium sulphides by Tronc and Huber (*10*). In order to test this possibility a number of crystals with different structures will have to be chemically analysed completely to determine if there is any composition variation involved. Polytypes will show no such variation. With respect to this latter point, attention can be drawn to the fact that Tronc and Huber (*10*) did not present analytical information about their samples, and there is no positive evidence that the crystals described by these authors are genuine polytypes.

The results presented here stress the importance of obtaining analytical data for individual crystals. X-ray powder photographs of the bulk and ground crystals from a sealed tube are usually identical, and on this basis one would consider the samples homogeneous. Therefore, analysis of the bulk noncrystalline material in the tube, and extrapolation to the single crystals present is not reliable and if at all possible the analytical information should be obtained on crystals which have also been studied in the electron microscope. In the present samples, crystal yields were too small to carry out individual analyses, and the plate-like habit of all crystals does not allow different phases to be separated optically with any certainty.

In conclusion, one can say that a number of new structures have been found in the titanium–sulphur system in the neighbourhood of Ti_2S_3. The number of sulphur layers in a repeat unit seems able to vary from 7 to 16, although large ordered regions of these types have not been found. Present results do not allow conclusions to be drawn as to whether these new structures are due to impurities or whether they are polytypes of the previously reported phases. Experiments are now in progress to investigate these possibilities, as well as to extend the phase range covered to include the whole of the TiS to TiS_2 region.

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