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$(2H)_2$-$2C$ Type Superstructure of $TiS_{1.62}$, Determined by High-Resolution Electron Microscopy

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A superstructure of $TiS_{1.62}$ is determined by 100 kV high-resolution electron microscopy, in which the arrangement of metal vacancies is obtained from structure images. The crystal has monoclinic symmetry (pseudo-hexagonal) with lattice parameters $a = 11.9$, $b = 6.85$, $c = 11.5$ Å, and $\beta = 90°$. The space group is considered as $F2/m$. Metal vacancies are confined to every second metal layer and ordered within the partly filled metal layer, resulting in formation of a $(2H)_2$-$2C$ type of superstructure. The ordered metal vacancy layers are arranged in $2C$-type stacking sequence along the c axis, while sulfur atoms are arranged in $2H$-type stacking sequence along the c axis.

The titanium–sulfur system has a variety of structures in the range between TiS and TiS_2 (*1*). The structures consist of various stacking sequences of sulfur atoms as well as metal vacancies. In their structures, metal vacancies were considered in a random distribution within the partly filled metal layers (*2*). Moret *et al.* (*3, 4*) have observed diffuse scattering on $Ti_{1+x}S_2$ and assigned it to be due to short-range ordering of titanium atoms in the partly filled metal layers. The authors found by means of high-resolution electron microscopy (*5, 6, 7*) and X-ray diffraction (*8*) that, in the Ti_2S_3 phase, metal vacancies were confined to every second metal layer and ordered within the partly filled metal layers, resulting in formation of a superstructure. We showed that slight differences in chemical composition resulted in two kinds of superstructure, as observed in the Cr_2S_3 phase by Jellinek (*9*). $TiS_{1.46}$ has a $(4H)_2$-$4C$ type of superstructure with lattice parameters $a = 5.92$, $b = 10.3$, $c = 22.8$ Å, and $\beta = 90$, while $TiS_{1.51}$ has a $(4H)_3$-$6C$ type with lattice parameters $a = 10.3$, $b = 5.92$, $c = 34.9$ Å, and $\beta = 90°$. Both structures are built up of the $4H$-type stacking sequence of sulfur atoms, but they differ from each other with respect to the stacking periods of the ordered metal vacancy layers along the c axis. The $(4H)_2$-$4C$ superstructure consists of 4-ordered metal vacancy layers, while the $(4H)_3$-$6C$ superstructure consists of 6-ordered metal vacancy layers. In this system, the characteristic is that the structures contain various kinds of stacking se-

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quences of sulfur atoms. It is therefore expected to find various kinds of superstructures related with different types of stackings of sulfur atoms.

In the present study, we try to observe a new superstructure of $TiS_{1.62}$ (Ti_5S_8) by 100 kV high-resolution electron microscopy, where the arrangement of metal vacancy layers is known directly from structure images.

The crystals were prepared by reduction with mixtures of H_2S and H_2 gases of crystals starting with compositions near TiS_2. The procedure for preparing the present crystals will be described elsewhere by one of the present authors (*10*). The composition of the obtained polycrystals was found to be $TiS_{1.62}$. The crystals were crushed in an agate mortar to fragments of several thousand angstroms. They were placed on a holey carbon-supporting film and observed by the 100 kV electron microscope (H-500). The images taken at underfocus of about 1000 Å were interpreted intuitively.

Figures 1a and b show electron diffraction patterns taken from $TiS_{1.62}$ crystal fragments, in which the incident electron beam was parallel to the [001] and [010] directions, respectively. Some of the reflexions are indexed on the basis of a NiAs subcell. The remaining spots exhibit the presence of a superstructure. They are situated at $h = m/2$, $k = n/2$, and $l = r/2$, where m, n, and r are integers. The lattice relations between the supercell and the NiAs subcell are $a = 4A_1 + 2A_2$, $b = 2A_2$, and $c = 2C$, where a, b, and c are lattice parameters for the supercell and A_1, A_2, and C for the NiAs subcell. The symmetry of the superstructure was monoclinic with lattice parameters $a = 11.9$, $b = 6.85$, $c = 11.5$ Å, and $\beta = 90°$, which are in good agreement with X-ray powder diffraction. The reduced cell is monoclinic with lattice parameters $a = 11.9$, $b = 6.85$, $c = 8.27$ Å, and $\beta = 134°$. The relation between the unreduced and reduced monoclinic cell is $a = a'$, $b = b'$, and $c = a' + 2c'$, where a', b', and c' are lattice parameters for the reduced cell. The systematic absent reflexions were $h + k = 2n + 1$ for hkl and $h = 2n + 1$ for $h0l$. The possible space groups are therefore Cm, $C2$, and $C2/m$. In this paper, the unreduced monoclinic cell is used in comparison with the NiAs subcell.

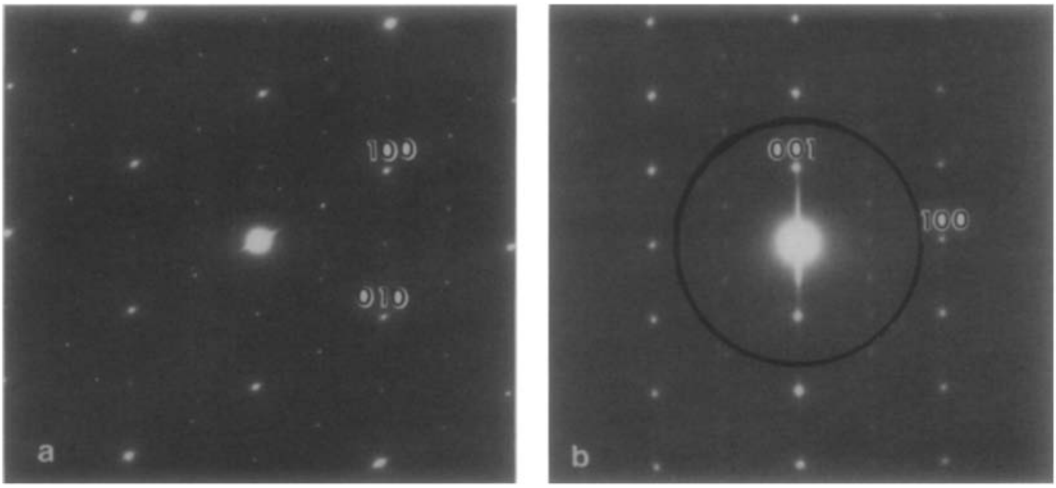

FIG. 1. Electron diffraction patterns from $TiS_{1.62}$ crystal fragments, taken with the incident electron beam parallel to the (a) [001] and (b) [010] directions. The indexed spots are based on the NiAs subcell.

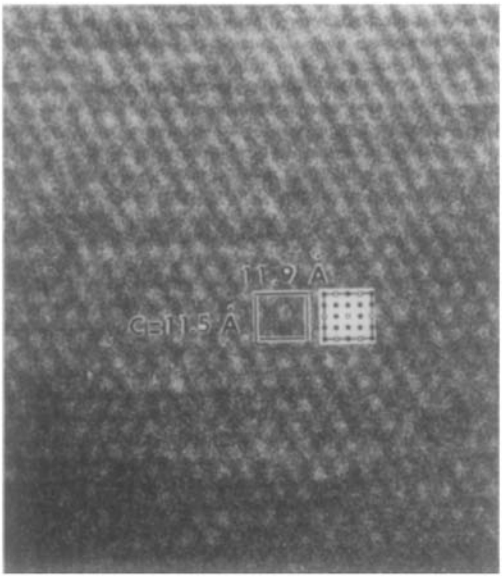

FIG. 2. A structure image obtained by the 100-kV high-resolution electron microscope. The corresponding diffraction pattern is shown in Fig. 1b, in which the position and the size of the objective aperture is outlined. A structure model is inserted into the figure, where open squares indicate the metal sites with vacancies and dark circles those without vacancies. the unit cell is outlined: a = 11.9, b = 6.85, c = 11.5 Å, and β = 90°.

Figure 2 shows a structure image from a very thin part of the crystal regions obtained by the 100 kV electron microscope. The corresponding diffraction pattern is shown in Fig. 1b, where the position and the size of the objective aperture is outlined. The size of the objective aperture corresponded to about 0.3 $Å^{-1}$ in reciprocal space. From the previous observations of titanium sulfides (*5–7*) and iron sulfides (*11*), it is shown that metal vacancy sites are imaged as white spots. Therefore, in this case, the white spots can be assigned as metal sites with vacancy. A structure model corresponding to the real image is shown in the inserted figure. It is then clear that a single metal site with vacancy is imaged as a single white spot in the present crystal.

The superstructure of $TiS_{1.62}$ projected onto the (010), (110), and (001) planes is shown in Figs. 3a, b, and c, respectively. The sites which are occupied by only half Ti atoms and those entirely occupied by Ti atoms are shown as open squares and dark circles in Figs. 3a and b, respectively. Sulfur atoms are abbreviated for simplicity in the figure. Circles *A*, *B*, *C*, and *D* represent one set of possible sites of titanium atoms within the partly filled metal layer. Metal vacancies are confined to every second metal layer and are ordered within the partly filled metal layers. Half of the metal sites are almost vacant in the present crystal. The stacking sequence of metal layers is represented as . . $V_A G V_C G V_A$ . . along the c axis, where V_A and V_C mean the defective metal layer and G is the completely filled metal layer. From the arrangement of titanium atoms as shown in Fig. 3a, the space group of the superstructure is considered as $F2/m$, which is identical with the space group of $C2/m$ for the reduced cell. The layers of sulfur atoms are interleaved with the complete and defective metal layers and line up in the stacking

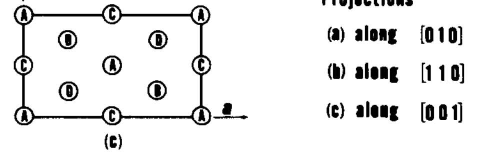

FIG. 3. A $(2H)_2$-$2C$ type superstructure of $TiS_{1.62}$. (a) and (b) show the superstructure projected onto the (010) and (110) planes, respectively. Open squares mean the sites which are occupied only half by Ti atoms and dark circles those entirely occupied by Ti atoms. (c) Circles *A*, *B*, *C*, and *D* mean possible sites of titanium atoms within the partly filled metal layer. Sulfur atoms are arranged in the $2H$-type, but they are omitted in the figure.

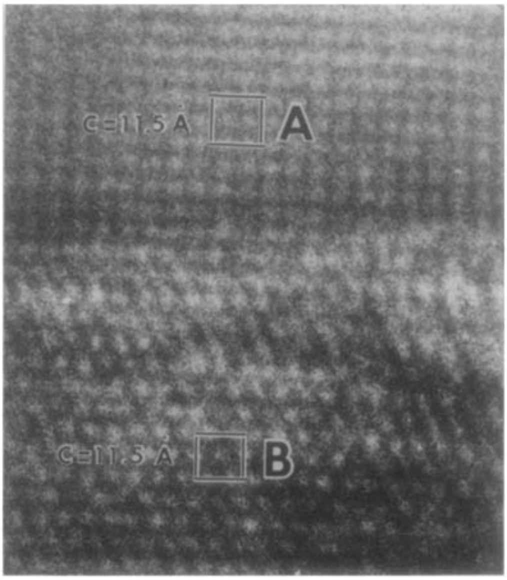

FIG. 4. The structure image showing the twin. The regions A and B correspond to the projections along [010] and [110], respectively. They are in twin relation of a 60 or 120° rotation along the *c* axis.

sequence . . $S_1S_2S_1$ . . (2*H*-type) along the *c* axis. Thus, the superstructure of $\mathrm{TiS}_{1.62}$ consists of four sulfur layers, two defective metal layers, and two completely filled metal layers. It can be represented as . . $V_AS_1GS_2V_CS_1GS_2V_A$ . . along the *c* axis. It is then called a $(2H)_2$-$2C$ type of superstructure in a combined representation of the arrangement of sulfurs and metal vacancies.

It is interesting to note in Fig. 4 that regions *A* and *B* correspond to the projections along the [010] and [110] as shown in Figs. 3a and b, respectively. Therefore it is clear that the regions A and B are in twin relation to one another with respect to a 60 or 120° rotation along the *c* axis.

The superstructure of the present crystal is identical with that of $\mathrm{VS}_{1.64}$ ($\mathrm{V_5S_8}$), where the crystal has monoclinic symmetry with lattice parameters $a = 11.396$, $b = 6.645$, $c = 11.293$ Å, and $\beta = 91.45°$ (*12*). In the Ti–S system, the structures of titanium sulfides whose compositions were near $\mathrm{Ti_5S_8}$ were previously described by Flink *et al.* (*13*) and Tronc and Huber (*14*). The former showed that sulfur atoms were arranged in 12*R*-type stacking, while the latter found that polytypes of the 12*H*-, 12*R*-, and 8*H*-types were formed. This means that $\mathrm{Ti_5S_8}$ crystallizes in different stackings of sulfur atoms. The present study suggests that when a $\mathrm{Ti_5S_8}$ crystal is formed by reduction from $\mathrm{TiS_2}$ which already consists of 2*H*-type sulfur stacking, a structure inheritance persists to result in the formation of the present $(2H)_2$-$2C$ type. The relations between crystal structures and chemical compositions in $\mathrm{Ti_5S_8}$are now under study.

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