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# X-ray structure analysis and electron density distributions of the layered compounds $\text{Cu}_x\text{TiS}_2$

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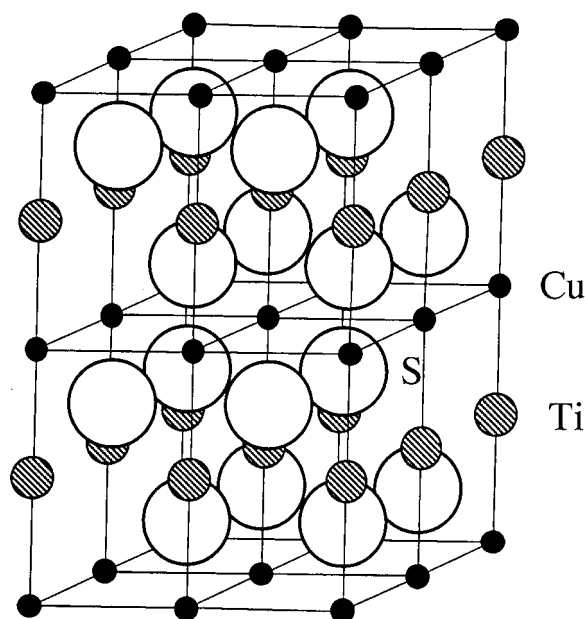
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## Abstract

X-ray structure analysis of single crystals of the  $\text{Cu}_x\text{TiS}_2$ , which were prepared by the iodine transport and the electrochemical methods, has been performed at room temperature. The structure of the samples prepared by the electrochemical method remains that of the mother crystal  $\text{TiS}_2$ , i.e. a layered compound. The other samples prepared by the iodine transport method have a spinel structure without a layered structure. Cu atoms in the  $\text{Cu}_x\text{TiS}_2$  made by this method tend to occupy tetragonal sites. This means that the electrochemical method is an effective method for the preparation of the layered compounds  $\text{Cu}_x\text{TiS}_2$ . The electron density distributions for the layered compounds by the maximum entropy method reveal that covalent bonding exists between the Ti and S atoms. On the other hand, no covalent electrons are found between Cu and S atoms. It is understood that Cu atoms show ionic character in these layered compounds.

## 1. Introduction

The transition metal dichalcogenides  $\text{TX}_2$  ( $T =$  transition metal,  $X = \text{S, Se, Te}$ ) with layered structures are normally separated by the van der Waals interaction. They are constructed by three sheets, i.e., one metal (M) sheet and two chalcogen (X) sheets, in which metal atoms M are sandwiched between two chalcogen sheets. In these compounds, various ions and molecules are intercalated between X layers. The intercalation compounds are of interest because of their low-dimensional properties [1, 2] and application as a high-density energy battery [3]. For  $\text{M}_x\text{TiS}_2$  ( $M = 3d$  metals), the inter-layer spacing  $c$  changes variously, while the intra-layer spacing  $a$  does not change drastically for the whole range of composition [4]. Here, the space group of the host structure  $\text{TiS}_2$  is  $P\bar{3}m1$  with trigonal symmetry. In fact, the lattice parameter  $c$  for single crystals of  $\text{Cu}_x\text{TiS}_2$  up to  $x = 0.61$  tends to increase with increasing  $x$ , while the in-plane lattice parameter is almost constant [5]. X-ray diffuse intensity



**Figure 1.** The structure of the layered compound  $\text{Cu}_x\text{TiS}_2$  ( $x = 1.0$ ). Cu atoms occupy the octahedral sites.

measurements show that two types of diffuse maxima due to the different in-plane correlations of Cu atoms appeared depending on the composition  $x$ . For the lower composition of Cu atoms ( $x = 0.13$ ), the maxima appeared at  $1/2 \ 0 \ 1/2$ ,  $0 \ 1/2 \ 1/2$ ,  $1/2 \ 1/2 \ 1/2$  and their equivalent positions. For the higher composition of Cu atoms ( $x = 0.37$ ), the maxima appeared at  $1/3 \ 1/3 \ 1/2$ ,  $2/3 \ 2/3 \ 1/2$  and their equivalent positions. In the cases of  $x = 0.23$  and  $0.32$ , two types of diffuse scattering coexist, with intensities depending on the composition [6].

Intercalated atoms between the layers of the van der Waals gap are capable of being positioned at the centres of the octahedra and the tetrahedra. The intercalant occupies the octahedral site in general [7]. In our previous study, the structure analysis was carried out by using a model in which the intercalated Cu atom was occupied at an octahedral site, as well as other layered compounds  $\text{M}_x\text{TiS}_2$  [8]. The crystal structure of  $\text{Cu}_x\text{TiS}_2$  ( $x = 1.0$ ) is shown in figure 1 for reference. The intercalation of Cu atoms was found to cause the expansion of these distances, and these atoms slightly change the structure of a mother crystal  $\text{TiS}_2$ . However, the analysis is still unclear about the occupancy of intercalated atoms.

In the present study, an x-ray structure analysis has been performed using two different models to reveal an atomic arrangement of intercalated Cu atoms in single crystals of the layered compound  $\text{Cu}_x\text{TiS}_2$  in detail. Furthermore, we have investigated the nature of the chemical bond of  $\text{Cu}_x\text{TiS}_2$  from the electron density distribution obtained by the maximum entropy method (MEM) [9–11]. This method enables us to obtain an electron density distribution directly from the observed structure factor.

## 2. Experimental details

The  $\text{TiS}_2$  single crystals were prepared by the iodine transport method in an evacuated quartz tube whose average size was about  $1 \times 1 \times 0.1 \text{ mm}^3$ . The  $\text{Cu}_x\text{TiS}_2$  single crystals were

**Table 1.** The experimental conditions for structure analysis.

Sample	1	2	3	4 (Spinel)
X-ray wavelength (Å)	0.5608	0.5608	0.5608	0.7107
<i>hkl</i> range				
<i>h, k</i>	−20 to 20	−10 to 10	−10 to 10	−19 to 19
<i>l</i>	−30 to 30	−30 to 30	−30 to 30	−19 to 19
Number of reflections				
measured	6802	4500	3170	7820
independent	576	455	321	222
Scan method	$2\theta-\omega$ scan	$2\theta-\omega$ scan	$2\theta-\omega$ scan	$2\theta-\omega$ scan
Scan width (deg)	$1.8 + 0.45 \tan \theta$	$1.9 + 0.45 \tan \theta$	$1.8 + 0.45 \tan \theta$	$1.2 + 0.3 \tan \theta$
Scan speed (deg/min)	6	6	3	6
Temperature (K)	295	295	295	295

prepared by two different methods. One is an electrochemical method. The single crystals of  $\text{Cu}_x\text{TiS}_2$  ( $x = 0.21, 0.38$ ) were prepared electrochemically by immersing  $\text{TiS}_2$  crystals in an aqueous solution of  $\text{CuSO}_4$  with Cu metal as an electrode [5]. These samples are designated by numbers 1, 2 and 3 in table 1. The other is a direct reaction method. The single crystal of  $\text{Cu}_x\text{TiS}_2$ , sample 4, was obtained by the following procedures. The powdered specimen of  $\text{TiS}_2$  was prepared by direct reaction of Ti and S powders in stoichiometric amounts in an evacuated quartz tube at 900 °C. The mixture of  $\text{TiS}_2$  and Cu powders in the evacuated quartz tube was located in the furnace at 1000 °C. The ratio of Cu to  $\text{TiS}_2$  was 1/3:1. The sample grew as a crystal with the polyhedron. Both  $\text{Cu}_x\text{TiS}_2$  samples thus obtained by two different methods changed colour from their original gold-metallic to black.

X-ray intensity data were collected at room temperature with the use of an automatic four-circle diffractometer where a flat graphite monochromator was utilized to obtain the Ag  $K\alpha$  radiation ( $\lambda = 0.5608 \text{ \AA}$ ) and Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). The experimental conditions for the present measurements are shown in table 1. Further, the composition of the samples was investigated with the use of electron probe micro-analysis (EPMA). The values were in good agreement with those obtained by the structure analysis.

Electron density distributions were reconstructed using MEM for  $\text{TiS}_2$  and  $\text{Cu}_x\text{TiS}_2$  ( $x = 0.21, 0.38$ ). Calculations were performed using the program MEED [12]. In this analysis, the data up to  $d_{\min} = 0.417, 0.416$  and  $0.437 \text{ \AA}$  were used in the MEM analysis, respectively. The number of independent reflections used for constraints were 320, 345 and 297 for the three specimens, respectively. The unit cell was divided into  $64 \times 64 \times 64$  pixels. The total number of electrons was calculated from the composition of the Cu atom obtained by the structure analysis. The reliability factor (*R*-factor) and the weighted reliability factor (*wR*-factor) range between 2.9–3.6% and 2.8–3.1%, respectively.

### 3. Results and interpretation

The structural analysis was performed assuming that Cu atoms occupied the octahedral and tetrahedral sites, respectively. The results of the analysis for sample 3 are shown in table 2. Because one and two atoms can occupy the octahedral and tetrahedral sites in a unit cell, respectively, the composition of the Cu atom of the tetrahedral model is consistent with the result of the octahedral model. However, the *R*-factor of the tetrahedral model is much larger than that of the octahedral model. The Cu atoms intercalated by the electrochemical method,

**Table 2.** The results of the analysis assuming that the Cu atoms occupy the octahedral and the tetrahedral sites.

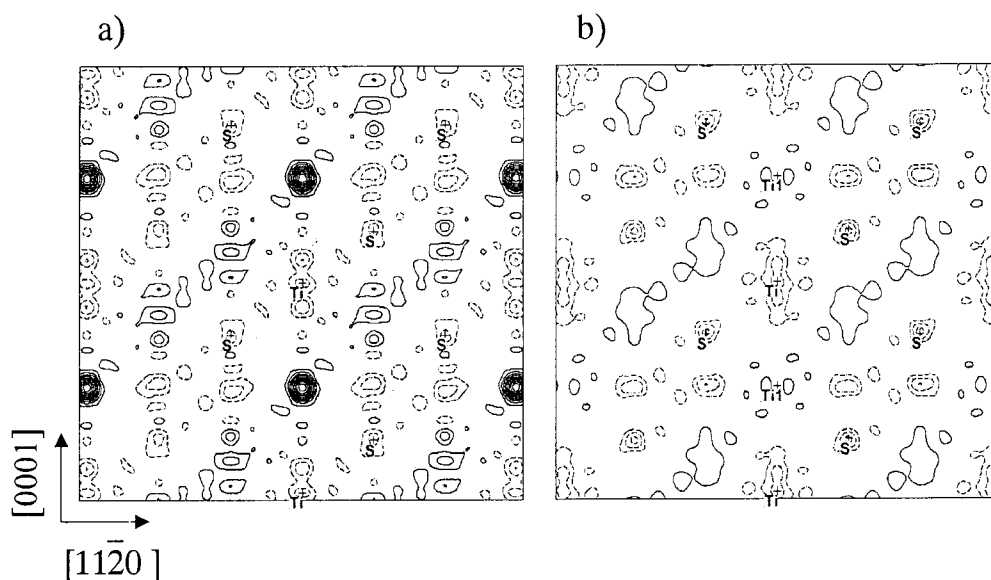
	Octahedral site	Tetrahedral site
$a = b$ (Å)	3.4146(15)	3.4146(5)
$c$ (Å)	5.8552(26)	5.8552(26)
Cu composition	0.384(2)	0.36(4)
$z$ (Cu)	0.5	0.526(5)
$z$ (S)	0.24629(6)	0.2451(6)
$U_{11}$ (Cu) ( $10^{-2}$ Å <sup>2</sup> )	3.04(4)	1.2(2)
$U_{33}$ (Cu) ( $10^{-2}$ Å <sup>2</sup> )	1.51(4)	6(2)
$U_{11}$ (Ti) ( $10^{-2}$ Å <sup>2</sup> )	1.032(8)	0.5(1)
$U_{33}$ (Ti) ( $10^{-2}$ Å <sup>2</sup> )	1.33(1)	1.6(1)
$U_{11}$ (S) ( $10^{-2}$ Å <sup>2</sup> )	0.834(8)	1.66(12)
$U_{33}$ (S) ( $10^{-2}$ Å <sup>2</sup> )	1.22(1)	0.6(1)
$R$ -factor (%)	3.3	28.1
w $R$ -factor (%) [ $w = 1/\sigma^2 F$ ]	3.2	32

therefore, occupy octahedral sites in the layer of the van der Waals gap. As shown in table 2, the temperature parameter of Cu atoms at the octahedral site,  $U_{11}$ , has a particularly large value compared with that of the Ti and S atoms, with the root-mean-square displacement of the Cu atoms equal to 0.174 Å. This clearly suggests that the vibration of the Cu atom at the average lattice site in the intercalated plane is large and indicates weak bonding.

Usually, no atoms exist in the layer of the van der Waals gap for a stoichiometric crystal of TiS<sub>2</sub>. However, as a few Ti atoms are intercalated in the layer for a real crystal, a structure analysis was carried out for a single crystal of TiS<sub>2</sub> using the program Xtal 3.4 [13] whether the self-intercalated Ti atoms exist or not. We have tried two structural models in the analysis; one has no Ti atoms and the other has an excess of Ti atoms in the layer of the van der Waals gap. The results are shown in table 3. For each atom, the value of  $U_{ij}$  in the stoichiometric TiS<sub>2</sub> model, i.e. the mean square displacement of atoms for the  $ij$  component, was in good agreement with those in the self-intercalated TiS<sub>2</sub> model. On the other hand, the  $R$ -factor of the self-intercalated TiS<sub>2</sub> model is smaller than that of the stoichiometric TiS<sub>2</sub> model. This means the self-intercalated TiS<sub>2</sub> model is more reasonable than the stoichiometric TiS<sub>2</sub> model. In fact, the real TiS<sub>2</sub> crystal is found to include 1.5% self-intercalated Ti atoms in the layer of the van der Waals gap. Figures 2(a) and (b) show the maps of the difference Fourier synthesis for the electron density distribution on the TiS<sub>2</sub> (11 $\bar{2}$ 0) planes. Contours in the figures start from  $-2.0$  e Å<sup>-3</sup> and are given at intervals of  $0.2$  e Å<sup>-3</sup>. The solid and dotted lines show the positive and negative values deviating from the spherical electron density distributions, respectively. The two spherical electron density distributions are estimated from the structure factor  $F$  of the stoichiometric TiS<sub>2</sub> and from that of the self-intercalated Ti<sub>1.015</sub>S<sub>2</sub>, respectively. No excess electron exists at the positions occupied by Ti and S atoms in figure 2(a). However, an electron density distribution is found at the octahedral site in the layer of the van der Waals gap in figure 2(a), though no atom occupies this site in the stoichiometric TiS<sub>2</sub>. This electron density distribution suggests that the stoichiometric TiS<sub>2</sub> model does not represent the structure of a real TiS<sub>2</sub>. On the other hand, an excess electron density distribution is not found in figure 2(b). This means that the self-intercalated TiS<sub>2</sub> model represents the experimental results quite well. This is consistent with the fact that the reliability factor in the self-intercalated TiS<sub>2</sub> model is smaller than that in the stoichiometric TiS<sub>2</sub> model.

**Table 3.** The results of the analysis of  $\text{TiS}_2$ . Ti1 means the self-intercalated Ti atom. Ti1, Ti and S atoms are located at  $(0, 0, 1/2)$ ,  $(0, 0, 0)$  and  $(1/3, 2/3, z)$ , respectively.

	$\text{TiS}_2$	$\text{Ti}_{0.015}\text{TiS}_2$
$a = b$ (Å)	3.4097(5)	3.4097(5)
$c$ (Å)	5.7052(5)	5.7052(5)
$z$ (S)	0.24872(6)	0.24872(6)
$U_{11}(\text{Ti})$ ( $10^{-2} \text{Å}^2$ )	1.24(1)	1.20(1)
$U_{33}(\text{Ti})$ ( $10^{-2} \text{Å}^2$ )	1.65(2)	1.64(1)
$U_{\text{eq}}(\text{Ti})$ ( $10^{-2} \text{Å}^2$ )	1.30(2)	1.29(1)
$U_{11}(\text{S})$ ( $10^{-2} \text{Å}^2$ )	0.944(10)	0.940(8)
$U_{33}(\text{S})$ ( $10^{-2} \text{Å}^2$ )	1.112(1)	1.11(1)
$U_{\text{eq}}(\text{S})$ ( $10^{-2} \text{Å}^2$ )	1.00(1)	1.00(1)
$U_{11}(\text{Ti1})$ ( $10^{-2} \text{Å}^2$ )	—	1.2(6)
$U_{33}(\text{Ti1})$ ( $10^{-2} \text{Å}^2$ )	—	1.6(9)
$U_{\text{eq}}(\text{Ti1})$ ( $10^{-2} \text{Å}^2$ )	—	1.4(8)
Ti1 composition		0.015(1)
R-factor (%)	2.46	2.13
wR-factor (%) [ $w = 1/\sigma^2 F$ ]	2.34	1.85

**Figure 2.** The maps of the difference Fourier synthesis for the electron density distribution on the  $\text{TiS}_2$  ( $1\ 1\ \bar{2}\ 0$ ) planes. Contours in the figures start from  $-2.0\ \text{e}\ \text{Å}^{-3}$  and are given at intervals of  $0.2\ \text{e}\ \text{Å}^{-3}$ . The solid and dotted lines show the positive and negative values deviating from the spherical electron density distributions, respectively. The spherical electron density distributions are estimated (a) from the structure factor  $F$  of the stoichiometric  $\text{TiS}_2$ , and (b) from the self-intercalation of  $\text{Ti}_{1.015}\text{S}_2$ .

The structure analysis was performed for  $\text{Cu}_x\text{TiS}_2$  ( $x = 0, 0.21, 0.38$ ). The self-intercalated Ti atoms were not considered in these analyses to simplify the comparison of the structural parameters of the three samples. We have assumed that only the Cu atoms were placed in the layer of the van der Waals gap. The results are shown in table 4. The inter-layer lattice constant  $c$  increases with increasing Cu composition, while the in-plane lattice constants  $a$  of

**Table 4.** Structural parameters obtained after the least squares fitting procedure.

Sample	1	2	3
$a = b$ (Å)	3.4097(5)	3.4145(6)	3.4146(15)
$c$ (Å)	5.7052(5)	5.8160(7)	5.8552(26)
Cu composition	0	0.2106(11)	0.384(2)
$z$ (S)	0.248 67(4)	0.247 12(3)	0.246 29(6)
$U_{11}$ (Cu) ( $10^{-2}$ Å <sup>2</sup> )	—	2.26(2)	3.04(4)
$U_{33}$ (Cu) ( $10^{-2}$ Å <sup>2</sup> )	—	1.21(2)	1.51(4)
$U_{11}$ (Ti) ( $10^{-2}$ Å <sup>2</sup> )	1.146(6)	1.136(4)	1.032(8)
$U_{33}$ (Ti) ( $10^{-2}$ Å <sup>2</sup> )	1.626(10)	1.365(6)	1.33(1)
$U_{11}$ (S) ( $10^{-2}$ Å <sup>2</sup> )	0.967(5)	0.921(4)	0.834(8)
$U_{33}$ (S) ( $10^{-2}$ Å <sup>2</sup> )	1.117(7)	1.111(6)	1.22(1)
$R$ -factor (%)	4.0	3.5	3.3
w $R$ -factor (%) [ $w = 1/\sigma^2 F$ ]	1.9	1.5	3.2

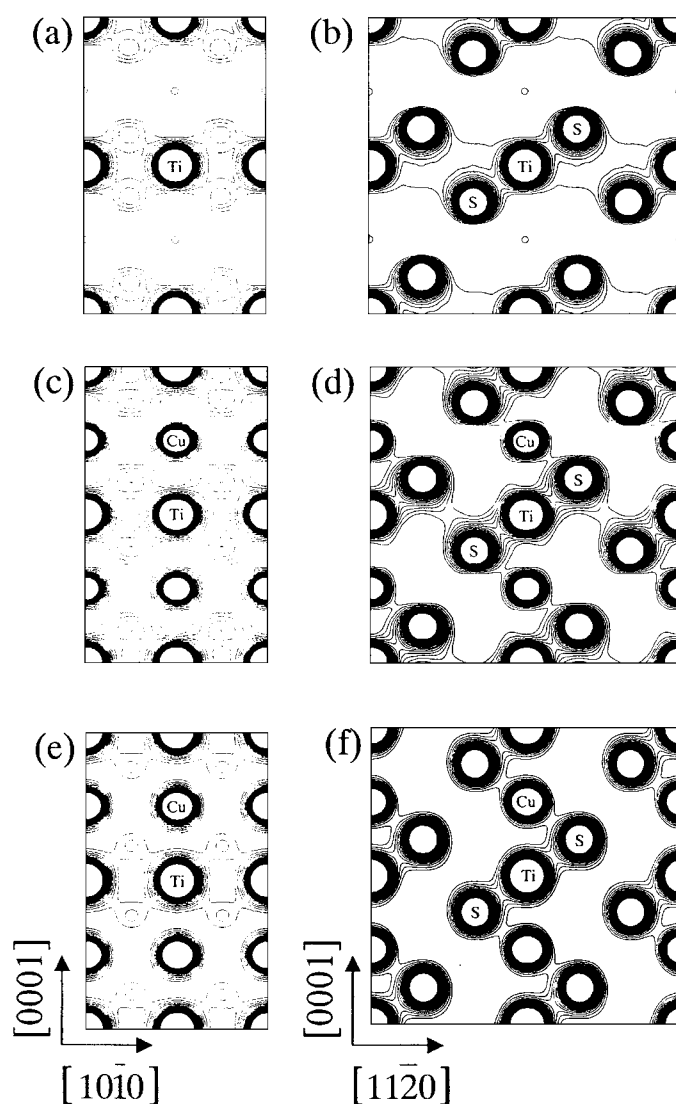
**Table 5.** Structural parameters of the spinel  $\text{Cu}_x\text{Ti}_2\text{S}_4$  prepared by the direct reaction method. Cu, Ti and S atoms are located at  $(1/8, 1/8, 1/8)$ ,  $(1/2, 1/2, 1/2)$  and  $(z, z, z)$ , respectively.

	Sample 4 (Spinel)
$a = b = c$ (Å)	9.9216(3)
Cu composition	0.652(3)
$x$ (S)	0.25429(1)
$U_{\text{eq}}$ (Cu) ( $10^{-2}$ Å <sup>2</sup> )	1.10(1)
$U_{\text{eq}}$ (Ti) ( $10^{-2}$ Å <sup>2</sup> )	1.354(8)
$U_{\text{eq}}$ (S) ( $10^{-2}$ Å <sup>2</sup> )	0.927(8)
$R$ -factor (%)	2.2
w $R$ -factor (%) [ $w = 1/\sigma^2 F$ ]	1.8

these three specimens are almost constant. The  $z$ -coordinate of the S atoms decreases with increasing Cu composition. The distance between the Ti-layer and the S-layer is obtained from the lattice constant  $c$  and the  $z$ -coordinate of the S atom of each sample and results in 1.219 Å, 1.437 Å and 1.442 Å for samples 1, 2 and 3, respectively. In addition, the intercalated Cu atoms enlarge the layer of the van der Waals gap. It is realized that the intercalation of Cu atoms causes expansion of the distance between the Ti- and S-layers as well as that of the layer of the van der Waals gap. The inter-layer displacement parameter  $U_{33}$  is larger than the in-plane parameter  $U_{11}$  for all three samples. The larger value of  $U_{33}$  is due to the weaker bonding along the  $c$ -axis than the in-plane axis. The square roots of  $U_{11}$  and  $U_{33}$  amount to about 3% of  $a$  and about 2% of  $c$ , respectively.

The data for sample 4 were analysed as having the spinel structure. The space group is  $Fd\bar{3}m$  with cubic symmetry. The structural parameters are shown in table 5. A lattice constant of this compound was obtained as  $a = b = c = 9.9216(3)$  Å. In this compound, Cu atoms are coordinated tetrahedrally and Ti atoms are coordinated octahedrally with S atoms as in other chalcogenide spinel compounds, such as  $\text{CuCo}_2\text{S}_4$ ,  $\text{CuRh}_2\text{S}_4$  and  $\text{CuIr}_2\text{S}_4$ .

The MEM electron density distributions of the  $(1\ 0\ \bar{1}\ 0)$  and  $(1\ 1\ \bar{2}\ 0)$  planes of  $\text{TiS}_2$  and  $\text{Cu}_x\text{TiS}_2$  ( $x = 0.21$  and  $0.38$ ), samples 1, 2 and 3, are shown in figure 3. Ti and the intercalated Cu atoms are located on the  $(1\ 0\ \bar{1}\ 0)$  plane, and Ti and S atoms are on the  $(1\ 1\ \bar{2}\ 0)$  plane, respectively. For  $\text{TiS}_2$ , it seems that a strong covalent bond exists between the Ti and S atoms in figure 3(b). On the other hand, the Ti–Ti and S–S bonds are found to be weaker than the

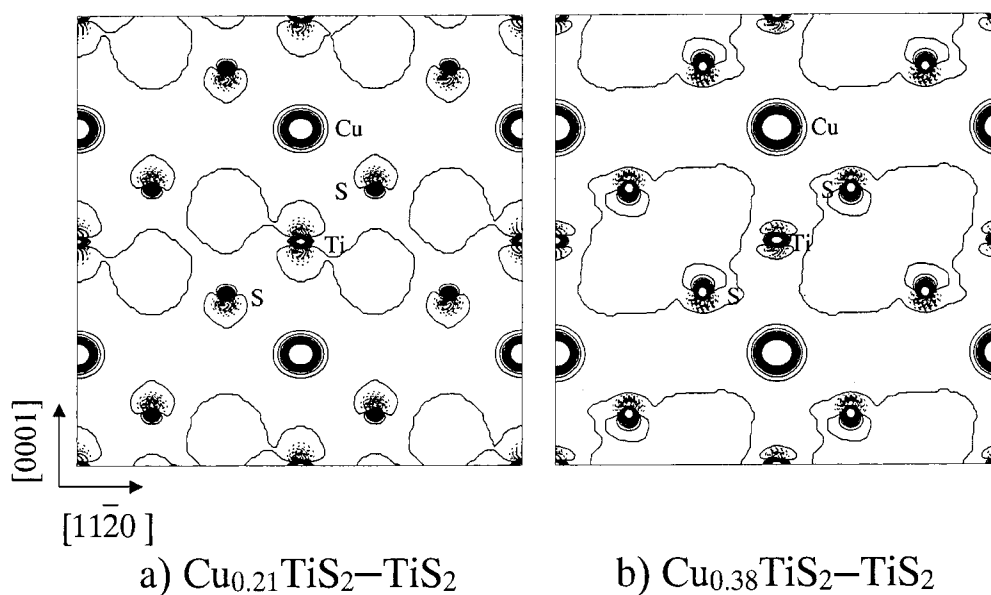


**Figure 3.** The MEM electron density maps of  $\text{TiS}_2$  (a) and (b),  $\text{Cu}_{0.21}\text{TiS}_2$  (c) and (d), and  $\text{Cu}_{0.38}\text{TiS}_2$  (e) and (f). The maps in (a), (c) and (e) are  $(1\ 0\ \bar{1}\ 0)$  planes, and those in (b), (d), and (f) are  $(1\ 1\ \bar{2}\ 0)$  planes. Contour lines are drawn from  $0.3$  to  $2.3\ \text{e}\ \text{\AA}^{-3}$  at  $0.05\ \text{e}\ \text{\AA}^{-3}$  intervals.

Ti–S bond (see figure 3(a)). The inter-layer S–S bond is also weak. For  $\text{Cu}_x\text{TiS}_2$ , the electron density distribution of the intercalated Cu atom was compared with that of  $\text{TiS}_2$ . Figures 3(d) and (f) show that a covalent bond exists between the Ti and S atoms as well as in figure 3(b). On the other hand, no extra electrons are found between the Cu and S atoms shown in figures 3(d) and (f). In other words, the intercalated Cu atoms are located as ionic atoms in the layer of the van der Waals gap and no covalent bond exists between the Cu and S atoms.

To find the effect of the intercalation of Cu atoms on the structure of layered compounds we carried out the subtraction of the MEM electron densities of  $\text{TiS}_2$  (sample 1) directly from those of  $\text{Cu}_{0.21}\text{TiS}_2$  (sample 2) and  $\text{Cu}_{0.38}\text{TiS}_2$  (sample 3). Figure 4 shows the difference in the electron density distributions thus obtained, where solid and dotted lines stand for positive and





**Figure 4.** The maps of the difference in the charge densities obtained by subtracting the MEM charge densities of  $\text{TiS}_2$  directly from those of  $\text{Cu}_{0.21}\text{TiS}_2$  and  $\text{Cu}_{0.38}\text{TiS}_2$ . Contours in the figures start from  $-10.0 \text{ e } \text{\AA}^{-3}$  with intervals of  $0.5 \text{ e } \text{\AA}^{-3}$ . Solid and dotted lines stand for the positive and the negative regions, respectively.

negative values, respectively. Contours in the figures start from  $-10.0 \text{ e } \text{\AA}^{-3}$  with intervals of  $0.5 \text{ e } \text{\AA}^{-3}$ . The electron density distribution is found at octahedral sites in the layer of the van der Waals gap in figures 4(a) and (b). This distribution is derived from the intercalated Cu atom. Both positive and negative values are found at the S site in both maps. This means that the intercalation of the Cu atom affects the coordinates of the S atom in the layered compound. In the core region of S atoms, the positive region derives from the change of the  $z$ -coordinate of the S atom, because the  $z$ -coordinate of the S atom of the Cu-intercalated compound is smaller than that of  $\text{TiS}_2$ . The range of positive and negative values surrounding the Ti site suggests that the electron density distribution of Ti atoms in  $\text{Cu}_x\text{TiS}_2$  differs from that in  $\text{TiS}_2$ . The positive region at the Ti site means that the density in the core region of the Ti atom of  $\text{Cu}_x\text{TiS}_2$  is higher than that of  $\text{TiS}_2$ . In other words, the electron density surrounding the Ti atom of  $\text{TiS}_2$  widens compared with that of  $\text{Cu}_x\text{TiS}_2$ .

#### 4. Summary

Structure analyses of the single crystals of  $\text{Cu}_x\text{TiS}_2$  prepared by two different methods were performed. The compound with the spinel structure was obtained by the direct reaction method. The layered compound was not synthesized by this method. Therefore, the electrochemical method was used to obtain single crystals of the layered compound  $\text{Cu}_x\text{TiS}_2$ . The results of the structure analysis assumed two different sites of the intercalated Cu atoms and show that the Cu atoms tend to occupy octahedral sites in the layer of the van der Waals gap. The electron density distribution obtained by MEM gives information about the bondings between atoms, which we cannot obtain from the maps of the Fourier synthesis. It is understood that the intra-layer bonding between Ti–Ti and S–S atoms is stronger than the inter-layer bonding between Ti- and S-layers. The electron density distributions reveal that a covalent bonding

exists between the Ti and S atoms. On the other hand, no covalent electrons are found between Cu and S atoms, i.e., Cu atoms are ionic in these layered compounds. To synthesize the layered compounds without a change of their structure, it is required that the intercalated atoms have an ionic bond with the mother phase, e.g.  $\text{TiS}_2$ . We expect that comparison of the electron density distribution of the layered compounds with other intercalating atoms will enable us to discuss their characteristics more clearly.

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