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Tomoko Kusawake [a], Yasuhiko Takahashi [a] & Ken-Ichi Ohshima [a]

[a] Institute of Applied Physics, University of Tsukuba, Tsukuba, 305-8573, Japan

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Structural Analysis of the Layered Compounds Cu_xTiS_2

TOMOKO KUSAWAKE, YASUHIKO TAKAHASHI
and KEN-ICHI OHSHIMA

Institute of Applied Physics, University of Tsukuba, Tsukuba 305–8573, Japan

A structural analysis of single crystals of the layered compounds Cu_xTiS_2 (x=0, 0.21 and 0.38), which were prepared by the iodine transport and the electrochemical methods, has been performed by X-ray diffraction. The displacement parameters of Ti and S atoms along the c axis are larger than those along the a axis. 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. Both distances between Ti- and S-layers and between Cu- and S-layers are enlarged without changing the structure of the mother phase after intercalating Cu atoms.

Keywords: layered compound; structural analysis; Cu_xTiS_2; X-ray diffraction

INTRODUCTION

The layered disulfide of transition metals MS_2(M=transition metal) has a two-dimensional layered structure, in which the in-plane atoms have strong ionic/covalent bondings. As a weak van der Waals force holds the structure

loosely between the layers, various ions and molecules are intercalated between the layers. After intercalation, the inter-layer spacing c changes variously, while the intra-layer spacing a does not change drastically for a whole range of composition. Lattice parameters of M_xTiS_2 (M=3d metals) obtained by X-ray diffraction were reported by Inoue *et al.*[1], but there are few reports on Cu_xTiS_2, especially with the use of single crystals. Here, the space group of the structure TiS_2 is $P\bar{3}m1$ with trigonal symmetry. As Cu atoms are intercalated between the sulfur layers randomly, the Cu_xTiS_2 shows the same space group as TiS_2. We have prepared single crystals of Cu_xTiS_2 by our new method[2] and performed an X-ray diffraction study to examine the in-plane arrangement of Cu atoms[3]. The observation of diffuse scattering reveals that the intercalated Cu atoms have peculiar short-range orderings in the van der Waals gap, with a three-dimensional nature. It is expected that Cu atoms are arranged with $\sqrt{3}\times\sqrt{3}$ and 2×2 in-plane structures at low temperature depending on the composition. On the other hand, information about the average structure is obtained by a conventional X-ray structural analysis. In the present study, we have done an X-ray structural analysis to investigate the effect on the structural parameters of Cu_xTiS_2 after intercalation.

EXPERIMENTAL

The TiS_2 single crystals were prepared by the iodine transport method. The

average size of the crystals was about $1 \times 1 \times 0.1 mm^3$. The single crystals of Cu_xTiS_2 (x=0.21 and 0.38) were prepared electrochemically by immersing TiS_2 crystals in an aqueous solution of $CuSO_4$ with Cu metal as the electrode. 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-Kα radiation (λ=0.5608Å). The experimental conditions for the present measurement are shown in Table I . In the experiment we have prepared three specimens #1, #2 and #3, with the compositional parameter x=0, 0.21 and 0.38, respectively.

TABLE I Experimental parameters for the present measurement

	#1	#2	#3
hkl range	-20≦h,k≦20 -30≦l≦30	-10≦h,k≦10 -30≦l≦30	-10≦h,k≦10 -30≦l≦30
number of reflections			
measured	6802	4500	3170
independent	576	455	321
collimator (mmϕ)	1	1	1
slit width (°)	3/4	3/4	3/4
scan method	2θ - ω scan	2θ - ω scan	2θ - ω scan
scan width (°)	1.8+0.45tanθ	1.9+0.45tanθ	1.8+0.45tanθ
scan speed (° / min)	6	6	3
temperature (K)	295	295	295

RESULTS AND DISCUSSION

The structural parameters were determined using the program *Xtal* 3.4 [4],

whereby all measured reflections were used. Assuming the intercalated Cu atoms to be occupied at octahedral sites, the structural analysis was performed by the least squares fitting procedure. The results of the analysis are shown in Table II. The reliability factor (R-factor) and the weighted reliability factor (wR-factor) range from 3.5-4.5% and 1.5-3.1%, respectively.

TABLE II The refined structural parameters obtained by the least-squares fitting procedure. Cu, Ti and S atoms are located at (0,0,1/2), (0,0,0) and (1/3,2/3,z). $U_{11}=U_{22}$, $U_{12}=U_{11}/2$, $U_{23}=U_{13}=0$. In this study, the temperature factors are defined as $\exp\left\{-2\pi^2\sum_{ij}h_ih_ja_i^*a_j^*U_{ij}\right\}$.

	#1	#2	#3
$a = b$ (Å)	3.4097(5)	3.4146(5)	3.4146(5)
c (Å)	5.7052(5)	5.816(7)	5.8552(26)
Cu composition	0	0.2106(11)	0.3752(35)
z (S)	0.24867(4)	0.24712(3)	0.24635(5)
U_{11}(Cu) (10^{-2} Å^2)	------	2.26(2)	3.04(4)
U_{33}(Cu) (10^{-2} Å^2)	------	1.21(2)	1.59(3)
U_{11}(Ti) (10^{-2} Å^2)	1.146(6)	1.136(4)	1.101(9)
U_{33}(Ti) (10^{-2} Å^2)	1.626(10)	1.365(6)	1.421(13)
U_{11}(S) (10^{-2} Å^2)	0.967(5)	0.921(4)	0.878(9)
U_{33}(S) (10^{-2} Å^2)	1.117(7)	1.111(6)	1.272(13)
R-factor (%)	4.0	3.5	4.5
wR-factor (%)	1.9	1.5	3.1

The c-axis lattice constant increases gradually with an increase of x, while the length of the a-axis one remained almost constant[2]. Fig.1 shows the Cu composition dependence of the distances between Ti- and S-layers, and between Cu- and S-layers (van der Waals gap layers), which are calculated

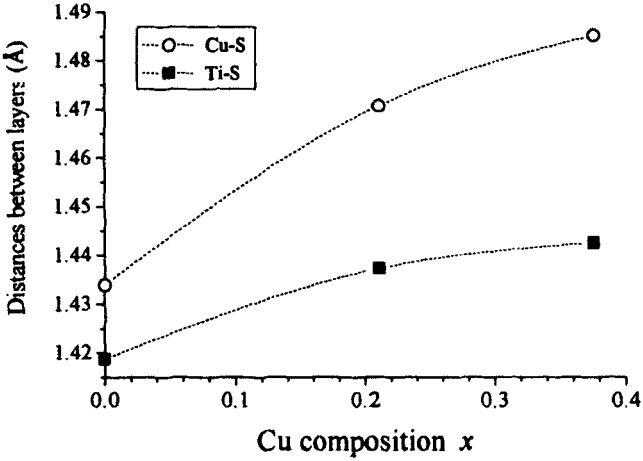

FIGURE 1 The Cu composition dependence of distances between Ti- and S-layers, and between Cu- and S-layers (van der Waals gap layers)

from the lattice constant *c* and the z-coordinate of the S atoms. Both distances increase with increasing x, compared to those of pure TiS_2. This means that the intercalation of Cu atoms causes the expansion of these distances. In $Ag_{0.18}TiS_2$ structure, similar result was obtained for the distances of Ag-S and Ti-S layers; the distance of Ti- and S-layers expanded from 1.42Å to 1.45Å after intercalation[5]. It is also clear that the ratio of the expansion of the distance between Cu- and S-layers is larger than that between Ti- and S-layers. It is understood that the intercalated Cu atoms affect the distance between Ti- and S-layers due to an effective repulsive interaction between Cu and Ti through

the S-layer.

The values of the displacement parameters U_{ij} were obtained. U_{ij} is equal to the mean square displacement of atoms for *ij* component. For Ti and S atoms, the inter-plane displacement parameter U_{33} is larger than the in-plane one U_{11} for all three specimens. The square roots of U_{11} and U_{33} are 0.09-0.11 and 0.11-0.13Å, which amount to about 3% of the lattice constant *a* and about 2% of *c*, respectively. The larger value of U_{33} means that the bonding along c-axis is weaker than the in-plane one. Anisotropy of the displacement parameter is due to the two-dimensional structure, that is, strong ionic/covalent bondings for in-plane atoms.

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