

X-ray diffraction study of lattice parameters for layered compounds $M_x\text{TaS}_2$ (M=TI or In)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 4625

(<http://iopscience.iop.org/0953-8984/7/24/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 21:28

Please note that [terms and conditions apply](#).

X-ray diffraction study of lattice parameters for layered compounds M_xTaS_2 ($M = Tl$ or In)

T Takeda, S Yokozeki, K Yamamoto and K Ohshima
Institute of Applied Physics, University of Tsukuba, Tsukuba 305, Japan

Received 16 January 1995, in final form 10 March 1995

Abstract. The composition dependence of lattice parameters for layered compounds M_xTaS_2 ($M = Tl$ or In , $0 < x < 0.6$) has been determined by an x-ray diffraction method, in order to discuss the structural characteristics. Stage-2 and stage-1 phases for both compounds exist. A drastic change in the c -axis layer spacing was found for stage-1 $Tl_{0.465}TaS_2$, although there was no such anomaly in the composition dependence of the c -axis lattice parameter for In_xTaS_2 .

1. Introduction

The transition-metal dichalogenides TX_2 ($T =$ transition metals; $X = S$ or Se) can be intercalated by various metals and molecules between the sulphur or selenium layers, which are normally separated through the van der Waals interaction. These intercalation compounds are of interest because of their quasi-two-dimensional properties [1, 2] and because of their application as electrodes in cells [3]. In particular, some compounds show the phenomenon of staging; these intercalation compounds are formed through the periodic insertion of intercalated layers separated by n TX_2 layers, where n defines the stage index. It is widely observed for alkali-metal graphite intercalates.

Eppinga and Wiegers [4] described the synthesis and structure determinations of the compounds M_xNbX_2 and M_xTaX_2 ($M = In, Sn, Pb$ or Bi ; $X = S$ or Se); their results were compared with those of other investigators for the same compounds. The structures of Tl compounds, not prepared by them, were also discussed. They found four different structure types. In all structures, the transition metal is in trigonal-prismatic coordination by the chalcogen atoms, as in the $2H-TX_2$ polymorph. From their report, we have taken an interest in the structure of the Tl_xTaS_2 compound for various reasons. One is that the structure for $Tl_{0.5}TaS_2$ has the space group $P\bar{6}m2$ [4, 5] and the other is that the c -axis interlayer distance of $Tl_{0.65}TaS_2$ is twice that for the $Tl_{0.5}TaS_2$ structure [4, 6]. Shimada [7] has reported the existence of stage-2 Tl_xTaS_2 and the anomalous composition dependence of the lattice parameter in the stage-1 Tl_xTaS_2 phase. He has also tried to determine the structure of a stage-1 $Tl_{0.47}TaS_2$ single crystal and found partial ordering of intercalated Tl atoms. However, the structure of the stage-2 phase for Tl_xTaS_2 has not yet been determined because it is difficult to prepare good single crystals.

In this report, we concentrate on obtaining the detailed composition dependence of lattice parameters for stage-2 and stage-1 Tl_xTaS_2 compounds by x-ray powder diffraction methods, because Shimada [7] did not show whether a variation in the c -axis parameter of Tl content in the stage-1 phase is continuous or critical at some concentration. Here we interpret the composition dependence of the c -axis parameter using a model based on the overlapping wavefunctions of Tl atoms. In contrast, Shimada [7] discussed the result using

the packing hard spheres of the constituent ions. The composition dependence of the lattice parameters for In_xTaS_2 compounds has also been determined, to compare with the results for the Tl_xTaS_2 compounds.

2. Experimental details and results

Seven powdered samples of Tl_xTaS_2 and 12 powdered samples of In_xTaS_2 were prepared by heating the pre-reacted TaS_2 powder and M (M = Tl or In) metal in an evacuated quartz tube at 700°C for 1 week. X-ray powder patterns were observed with an ordinary diffractometer at room temperature to obtain the *a*- and *c*-axis lattice parameters using Cu $K\alpha$ radiation (whose wavelength is 1.54178 Å generated from an x-ray sealed tube, where the 2θ scan range was from 5 to 75°. Diffraction patterns were also measured from -5 to -25° to correct the exact zero for the 2θ angle.

Table 1. Tl content dependence of the *c*-axis lattice parameter for Tl_xTaS_2 compounds. The accuracy of the parameters was determined to within 0.05 Å.

Tl content	<i>c</i> -axis lattice parameter (Å)	Stage
0.25	14.74	2
	8.72	1
0.35	8.68	1
0.45	8.63	1
0.465	8.11	1
0.485	8.10	1
0.55	8.06	1
0.60	8.06	1
0.0 (2H-TaS ₂)	12.17	

Table 2. In content dependence of the *c*-axis lattice parameters for In_xTaS_2 compounds. The accuracy of the parameters was determined to within 0.05 Å.

Tl content	<i>c</i> -axis lattice parameter (Å)	Stage
0.10	13.86	2
0.15	13.91	2
0.20	13.95	2
0.25	13.83	2
0.30	13.88	2
0.35	14.05	2
	7.99	1
0.40	13.84	2
	7.99	1
0.45	7.98	1
0.50	7.94	1
0.55	7.95	1
0.60	7.96	1
0.67	7.92	1

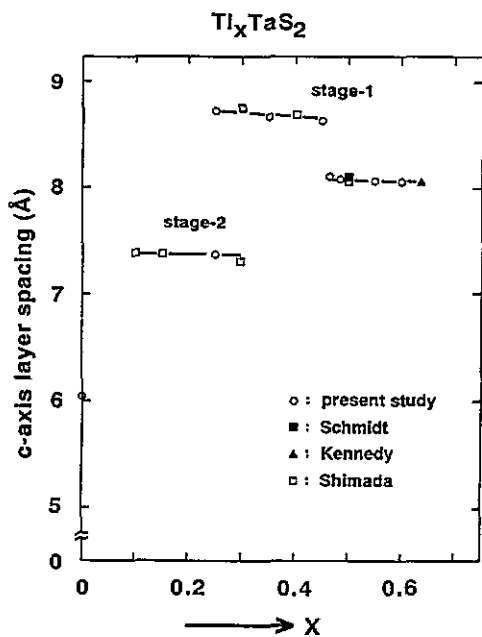


Figure 1. Tl content dependence of the c -axis layer spacing of Tl_xTaS_2 compounds. The c -axis layer spacing for the stage-2 phase is half the c -axis lattice parameter.

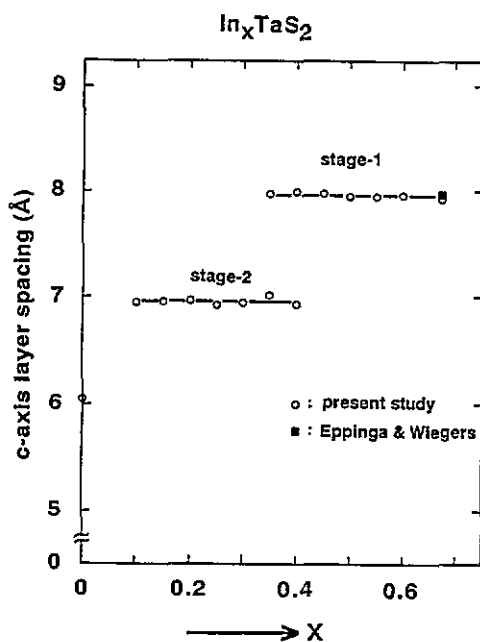


Figure 2. In content dependence of the c -axis layer spacing of In_xTaS_2 compounds. The c -axis layer spacing for the stage-2 phase is half the c -axis lattice parameter.

After analysing the diffraction patterns, both a -axis and c -axis lattice parameters were determined for 19 powdered specimens. The lattice parameters for a powdered 2H-TaS₂ specimen were also obtained. The a -axis lattice parameter is independent of composition and given as 3.315 ± 0.015 Å for all the specimens. The c -axis lattice parameters for Tl_xTaS_2 and In_xTaS_2 compounds are given in tables 1 and 2, respectively. In these measurements, the accuracy of lattice parameters was determined to within 0.05 Å. The composition dependences of the c -axis layer spacing for Tl_xTaS_2 and In_xTaS_2 are shown in figures 1 and 2, respectively, in which the c -axis layer spacing for stage-2 phase is half the c -axis lattice parameter. In fact, stage-2 and stage-1 phases for both compounds do exist, as Shimada [7] has already reported, in particular, for Tl_xTaS_2 . The values of the c -axis layer spacing obtained previously are also depicted in the figures. The agreement between them is quite good. The Tl content ranges for stage-2 and stage-1 phases of Tl_xTaS_2 in figure 1 are from 0.1 to 0.25 and from 0.30 to 0.60, respectively. The value of the c -axis layer spacing does not change in the composition region of the stage-2 phase. For the region of the stage-1 phase, first the c -axis layer spacing slightly decreases with increasing Tl content, then drastically decreases at $x = 0.465$ without any structural change and finally remains constant with further increase in the Tl content. A brief interpretation of this peculiar characteristic will be given in the next section.

The In content ranges for stage-2 and stage-1 phases of In_xTaS_2 are from 0.1 to 0.35 and from 0.40 to 0.67, respectively. The values of the c -axis layer spacing are independent of the In content in both phases. Further, we have observed that there is no drastic change in the region of the stage-1 phase.

3. Discussion

It is characteristic that an abrupt change in the *c*-axis layer spacing at $\text{Tl}_{0.465}\text{TaS}_2$ without any structural change is observed. This specific feature has already been observed in the pressure dependence of the lattice parameter for face-centred cubic Ce metal [8]. A 17% decrease in volume followed near 550 K and 18 kbar without any structural change. This γ - α transition has been interpreted as due to hybridization effects of 4f-5d electrons [9, 10].

We now try to interpret the structural meaning of the drastic change in *c*-axis layer spacing in the stage-1 phase for Tl_xTaS_2 compounds. Although Shimada [7] has discussed it using a model based on the packing hard spheres of constituent ions, here we propose another idea. The outer shell of electrons for Tl atoms is usually expressed as $6s^26p^1$. In a composition range from a low Tl content to $x = 0.465$, it is thought that the intralayer electrons of intercalated Tl atoms do not overlap those of neighbouring Tl atoms. The Tl atoms will have their usual atomic or ionic radii. However, above $x = 0.465$, the intralayer electrons of the Tl atoms have a chance to overlap those of neighbouring atoms owing to the higher Tl atom content. Because of this effect, the shape of the electron density distribution becomes elliptical and the value of the *c*-axis layer spacing contracts drastically. On the other hand, the *c*-axis layer spacing of the stage-1 In_xTaS_2 will be controlled by the atomic or ionic radii of In atoms, which is smaller than that of Tl atoms. Even if the In atom content increases, the *c*-axis layer spacing in the stage-1 phase does not change.

This is a very simple interpretation of the drastic change in the *c*-axis layer spacing in the stage-1 phase of Tl_xTaS_2 compounds, compared with that for In_xTaS_2 compounds. To confirm the above, an accurate electron density distribution in the stage-1 phase of Tl_xTaS_2 with $x = 0.465$ will be determined using an x-ray single-crystal structural analysis.

Acknowledgments

The authors would like to thank Mr M Shimada and Dr Y Kashihara for their helpful discussions and Professor H Iwasaki for informing us of the references on Ce metal.

References

- [1] Ohshima K and Moss S C 1983 *Acta Crystallogr. A* **39** 298
- [2] Kuoriwa Y, Ohshima K and Watanabe Y 1990 *Phys. Rev. B* **42** 11 591
- [3] Wieggers G A, Bouwmeester H J M and Gerards A G 1985 *Solid State Ion.* **16** 155
- [4] Eppinga R and Wieggers G A 1980 *Physica B* **99** 121
- [5] Schmidt V 1971 *Dissertation* University of Tübingen
- [6] Kennedy R T 1978 *Dissertation* University of Fordham
- [7] Shimada M 1984 *Dissertation* Nagoya University (in Japanese)
- [8] Davis B L and Adams L H 1964 *J. Phys. Chem. Solids* **25** 379
- [9] Fujimori A and Weaver J H 1985 *Phys. Rev. B* **32** 3422
- [10] Min B I, Jansen H J F, Oguchi T and Freeman A J 1986 *Phys. Rev. B* **34** 369