Journal of Alloys and Compounds 317–318 (2001) 284–286

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Crystal structure of Zr_2CuSb_3 and related compounds

N. Koblyuk[a,*], G. Melnyk[a], L. Romaka[a], O.I. Bodak[a], D. Fruchart[b]

[a] *Chemistry Department, I. Franko University, Kyryl and Mephodiy str. 6, Lviv, Ukraine*
[b] *Laboratoire de Cristallographie, CNRS, BP 166, 38042 Grenoble Cedex 9, France*

Abstract

The refinement of the crystal structure of the Zr_2CuSb_3 compound was performed using X-ray diffraction data. It is the first representative of a new structure type of intermetallic compound. It is tetragonal, with space group SG $P\text{-}4m2$, and with cell parameters $a=3.9404(1)$ Å, $c=8.6971(2)$ Å. Isostructural compounds were found in the M–Cu–Sb systems with M=Ti and Hf and their structure was refined as well. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structure; Antimonides

---

1. Introduction

Study of the affinity and reaction at 770 K between the components of the M–Cu–Sb systems where M=Ti, Zr, Hf, leads to the discovery of new compounds having the approximate composition $M_{0.33}Cu_{0.17}Sb_{0.50}$. Analysis of the crystal structure of these materials by using X-ray powder diffraction techniques was required before the establishment of potential structural relationships with other ternaries and, then, the analysis of the metal atom coordinations.

2. Experimental

Samples were prepared by arc melting pieces of the constituent metals in an argon atmosphere. The starting element purities were of 99.93 wt% for titanium, zirconium and hafnium; 99.96 wt% for copper and of 99.99 wt% for antimony. After melting, the resulting buttons were annealled in quartz ampoules first evacuated, then argon gas filled, maintained at 770 K for 2 days and then water quenched.

The data collections used for the crystal structure determinations were recorded using a HZG-4A and a Siemens D-5000 powder diffractometers both equipped with CuKα radiation. The structure refinements were performed by using the DWB program [1].

3. Results and discussion

Detailed crystal structure investigations have been carried out on different compounds having the same nominal composition $M_{0.33}Cu_{0.17}Sb_{0.50}$ with M=Ti, Zr, Hf. The cell parameters of the tetragonal phases were determined in a first step, and they are reported in Table 1.

For the first attempts, the analysis of the structure was undertaken on the basis of the Cu_2Sb type (SG $P4/nmm$, $a=3.992$ Å, $c=6.091$ Å), to which both the general composition and the cell parameters can be roughly related, taking into account the differences in size of the elements. Moreover the observed extinction rules were found in agreement with the latter space group. The elemental composition was distributed on three different sites with for example, 2 Zr in 2c, 2 Sb in 2a and

Table 1
Summary of crystallographic data

Formula	Ti_2CuSb_3	Zr_2CuSb_3	Hf_2CuSb_3
Crystal system	tetragonal	tetragonal	tetragonal
Space group	$P\text{-}4m2$	$P\text{-}4m2$	$P\text{-}4m2$
a (Å)	3.9238(2)	3.9404(1)	3.9216(1)
c (Å)	8.6445(5)	8.6971(2)	8.5947(2)
Cell volume (Å^3)	133.09	135.04	132.18
Radiation used	Cu-Kα	Cu-Kα	Cu-Kα
Diffractometer	HZG-4A	Siemens D5000	HZG-4A
Number of atom sites	4	4	4
Number of free parameters	25	25	25
2θ range	20–140	15–144	15–139
Collected reflections	200	210	206
$R_F - R_I$	6.40–8.47	6.80–8.96	5.32–6.97

---

*Corresponding author.

0925-8388/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0925-8388(00)01349-9

Table 2
Comparison of the atom site distributions in the $P4/nmm$ and $P\text{-}4m2$ space groups

$P4/nmm$					$P\text{-}4m2$				
M	2c	0	1/2	*z*	M	2g	0	1/2	*z*
Sb	2c	0	1/2	*z*	Sb2	2g	0	1/2	*z*
(Cu,Sb)	2a	0	0	0	Cu	1a	0	0	0
					Sb1	1b	1/2	1/2	0

1(Cu+Sb) in 2a. Using a Rietveld type of procedure [1], the refinements yield too large *R*-factor values.

Splitting of the 2a position which was previously considered as statistically occupied by 0.5Cu+0.5Sb, leads us to take into consideration the SG $P\text{-}4m2$, which also fulfills the extinction rules. The corresponding refinements of the crystallographic structure retained the full occupation of a 2g site by M, a second 2g site by Sb (called Sb2), a 1a site by Cu and a 1b site by Sb (called Sb1). Table 2 contains the two sets of metal atom distributions referenced to the respective space groups mentioned here above. The second set of atom positions indicates a full ordering of the three different elements constituting the structure.

Quite reasonable agreement factors ($5.3<R_F<6.8$) were achieved when using the $P\text{-}42m$ description. Comparison of the crystal data and related measurements are reported in Table 1. The atomic parameters, the atom coordinations as well as the refined temperature factors are given in Table 3 for the three refined compounds with M=Ti, Zr and Hf.

Fig. 1 shows both the projection of the unit cell of the Zr_2CuSb_3 structure onto the *y*–*z* plane and the coordination polyhedra of the different atoms. The interatomic distances shorter than 3.1 Å are listed in Table 4.

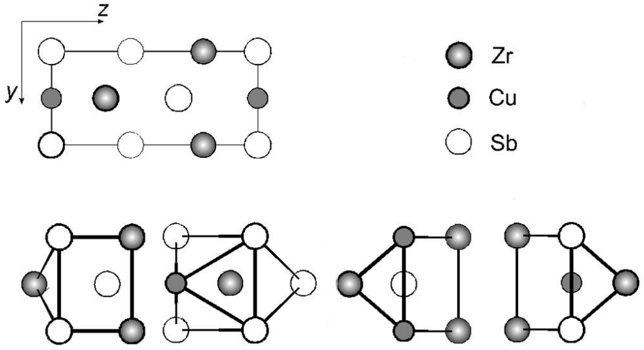

Fig. 1. Up: projection of the Zr_2CuSb_3 unit cell onto the *y*–*z* plane; down: coordination polyhedra of the different metal sites, from left to right Sb2 (2g), M (2g), Sb1 (1b), Cu (1a).

Table 3
M_2CuSb_3: atomic sites, position parameters and temperature factors

Atom	Cu in 1a	Sb1 in 1b	M=Ti, Zr, Hf in 2g	Sb2 in 2g
Ti_2CuSb_3				
x/*a*	0	1/2	0	0
y/*b*	0	1/2	1/2	1/2
z/*c*	0	0	0.7315(5)	0.3835(5)
Occupation	1	1	1	1
B_{iso} (Å^2)	0.50(5)	1.00(5)	0.55(5)	1.00(5)
Zr_2CuSb_3				
x/*a*	0	1/2	0	0
y/*b*	0	1/2	1/2	1/2
z/*c*	0	0	0.7365(5)	0.3835(5)
Occupation	1	1	1	1
B_{iso} (Å^2)	0.55(5)	0.85(5)	1.00(5)	0.90(5)
Hf_2CuSb_3				
x/*a*	0	1/2	0	0
y/*b*	0	1/2	1/2	1/2
z/*c*	0	0	0.7340(5)	0.3820(5)
Occupation	1	1	1	1
B_{iso} (Å^2)	0.50(5)	0.95(5)	0.95(5)	1.00(5)

In the presented compounds, the first example of a new type of ternary intermetallics, all of the three types of atoms do not exhibit close contact distances with the same one type of element as shown in Table 4. The first coordination shell of the Sb1 atom is unlikely made by metal element M and Cu, unlike that of the copper atom which has mixed coordination.

The Zr_2CuSb_3 crystal structure can be represented as the juxtaposition of double tetragonal antiprisms (1Zr.4Sb.2Cu.2Sb) and tetrahedral (4Sb) prisms as shown in Fig. 2. Another way to describe the structure is to consider two identical nets of Sb1 and M atoms relatively shifted each other by *a*/2, which are separated by square centered nets formed with Cu and Sb1 atoms as represented in Fig. 3.

A consideration of the Fe_2As structure is that it is a parent structure of the Cu_2Sb one [2], and is a reference to a general picture based on the description of the metal sites and lattices [3], the first coordination polyhedra of the elements are, respectively: for Fe1 (2a) a As-tetrahedron, for Fe2 (2c) a square based As pyramid, for As (2c) a

Table 4
Interatomic distances (Å) in the M_2CuSb_3 compounds

Atoms		Ti	Zr	Hf
Cu (1a)	4×Sb1 (1b)	2.775	2.786	2.773
	4×M (2g)	3.040	3.021	3.011
Sb1 (1b)	4×Cu (1a)	2.775	2.786	2.773
	4×M (2g)	3.040	3.021	3.011
M (2g)	4×Sb2 (2g)	2.948	2.976	2.948
	2×Cu (1a)	3.040	3.021	3.011
	2×Sb1 (1b)	3.040	3.021	3.011
	1×Sb2 (2g)	3.006	3.073	3.025
Sb2 (2g)	4×M (2g)	2.948	2.976	2.948
	1×M (2g)	3.006	3.073	3.025

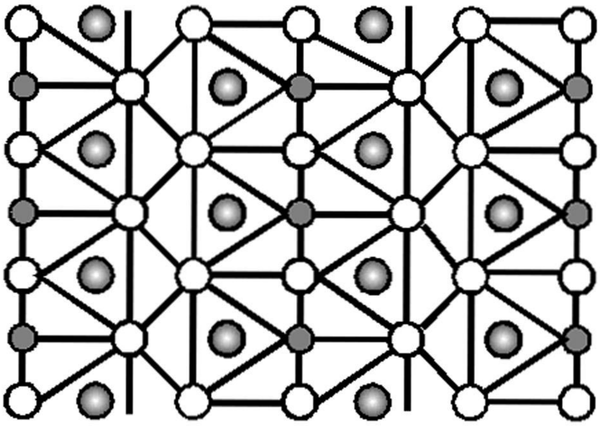

Fig. 2. Stacking of a bi-layer of tetragonal antiprism (1Zr.4Sb.2Cu.2Sb) and a mono-layer of Cu atoms.

triangular based prism of Fe plus three equatorial Fe. The location of the M1 and M2 in As (X: a p-element) four- and five-fold coordinations were analysed in terms of selective criteria such as the size and the relative electronegativity of the metal atoms [3]. Here, the situation is not exactly so well defined since the structure is built from similarly big atoms (except Cu) located in 2g (M and Sb) and in 1b (Sb). Nevertheless, for Cu and Sb1 it is possible to distinguish a tetrahedral environment formed with four M atoms, for Sb2 it is possible to consider a pyramidal environment formed with (4+1) M atoms, for M there is a nine-coordinated environment formed with (4+2) (Sb2+Sb1) and (2+1) (Cu+Sb2). From this rough analysis, one can see that here M (metal) takes a similar place as Sb (p-element) in Cu_2Sb, here Sb1 (p-element) is apparented to Cu2 (metal) in Cu_2Sb, Sb1 (p-element) and finally Cu (metal) is equivalent to Cu1 (metal) in Cu_2Sb. So, we can consider that the new Zr_2CuSb_3 is not exactly an ordered derivative of the Cu_2Sb type, but more realistically, should be considered as an anti-structure of the same prototype Cu_2Sb. A similar feature with the splitting of the 2a position of the Cu_2Sb structure (SG $P4/nmm$) in two positions 1a and 1b (SG P-4m2) was reported for Rh_3P_2 except that position 1b is vacant [4].

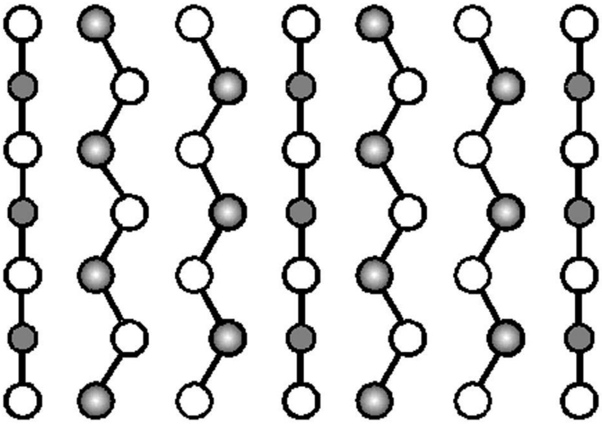

Fig. 3. Presentation of the new Zr_2CuSb_3 structure as mixed nets of Zr–Sb2 (2g sites) and of Cu–Sb1 (1a and 1b sites).

In a forthcoming paper, we will analyse the characteristics of the new Zr_2CuSb_3 type in terms of electronic band structure calculations.

Acknowledgements

N.K thanks the French CIES organisation for its financial support over a 3-month period in Grenoble.

References

[1] R.A. Young, A. Sakthivel, T.S. Moss, C.O. Pavia-Santos, Program DBW 9411 for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns, Georgia Institute of Technology, Atlanta, 1995.

[2] M. Elander, G. Haggland, A. Westgren, Arkiv für Kemi, Mineralogi och Geologi 12B (1935) 1.

[3] R. Fruchart, Ann. Chimie 6–7 (1982) 563.

[4] E.H. El Ghadraoui, 3C. Thesis, University of Rennes, France, 1982.