X-Ray Studies in the System Ti–Hg–Zn

M. Pušelj and Z. Ban

Institute for Inorganic and Analytical Chemistry,
the University Zagreb, Yugoslavia

(Z. Naturforsch. **25 a**, 315 [1970]; received 5 January 1970)

In a recent paper reported on part of the system Ti-Cu-Hg[1] a new phase $TiCuHg_2$ was found having the crystal structure B 32 (NaTl type). The most interesting but hitherto unexplained feature of this structure is the degree of filling of the unit cell (71%). In order to examine which one of the metals in the structure is eventually responsible for the formation of this particular phase, to which often a certain degree of ionic bonding is ascribed[2], we tried to prepare the isostructural compound $TiZnHg_2$. However, it turned out that its crystal structure belongs to the $AuCu_3$ (Ll_2) type ($a = 4.02 \pm 0.02$ Å), where all atoms are distributed statistically. We assume that the alternative configurations of the electron shells in the copper atom ($3d^{10}4s^1$ or $3d^94s^2$) may be responsible for such a behaviour. Diffractometer data for this phase are given in Table I.

HKL	d_0	d_c	I_0	I_c
111	2.310	2.320	100	100
200	2.010	2.013	40	45
220	1.425	1.421	38	40
311	1.212	1.210	42	45
222	1.164	1.160	15	14
400	1.002	1.002	5	8
331	0.923	0.923	20	18
420	0.897	0.897	25	23
422	0.821	0.821	25	20
$\varrho_X = 13.05$ g/cm^3, $\varrho_0 = 12.19$ g/cm^3				

Table I. Diffractometer data for $TiZnHg_2$ (CuKα-radiation) (Ll_2-type).

We also found that exactly 25% of titanium atoms in the TiHg phase (L I_0-AuCu type)[3] can be replaced by zinc, yielding thus a continuous series of solid solutions $TiHg$-Ti_3Hg_4Zn. It is interesting to notice that the zinc atoms tend to occupy preferentially positions parallel to the basal plane of the tetragonal unit cell of Ti_3Hg_4Zn ($a = 4.14 \pm 0.02$ Å, $c = 4.04 \pm 0.02$ Å). Since they are smaller than titanium atoms ($r_{Ti} = 1.47$ Å, $r_{Zn} = 1.34$ Å) parameter a decreases monotonously (Fig. 1) while c remains constant within the error limits. We were unable to find any sign of ordering between the zinc and titanium atoms in the intermediary layer, even though an extensive series of experiments has been carried out. The relevant x-ray (film) data are given in Table II.

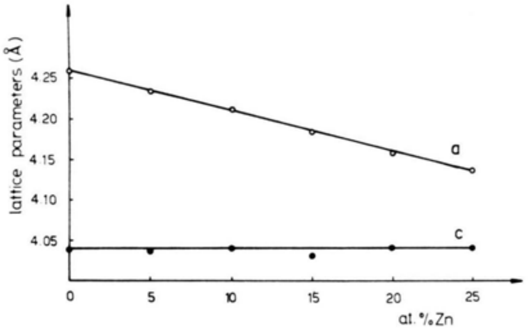

Fig. 1. The variation of the lattice parameters a and c in the series of solid solutions $TiHg$-Ti_3ZnHg_4.

HKL	d_0	d_c	I_0	I_c
001	4.031	4.041	20	19
110	2.936	2.934	22	20
111	2.372	2.375	100	100
200	2.072	2.069	30	22
201	1.844	1.844	14	11
112	1.663	1.667	16	14
220	1.462	1.464	12	10
221	1.373	1.376	6	4
003	1.350	1.351	1	2.10^{-3}
310	1.308	1.308	2	4
311	1.245	1.242	15	8
222	1.188	1.186	6	8
203	1.127	1.129	1	2
312	1.100	1.099	1	3
004	1.010	1.009	1	0.4
114	0.995	0.954	1	2
311	0.948	0.948	6	2
420	0.924	0.923	3	1
422	0.845	0.844	5	2
$\varrho_X = 12.15$ g/cm^3 $\varrho_0 = 11.80$ g/cm^3				

Table II. X-ray data for Hg_4ZnTi_3 (CuKα-radiation).

Samples were prepared by heating mixtures of the elements in Vycor tubes filled with purified and dried argon (0.5 at.) at temperatures ranging from 400 – 700 °C, depending on composition. Densities were determined pycnometrically at least three times for each particular sample, using decalin, CCl_4 and CH_2J_2. The observed discrepancies must be ascribed to the pasty nature of the samples and the very pronounced tendency towards decomposition, during extended aging at room temperature.

Reprints request to Dr. Z. Ban, Institute for Inorganic and Analytical Chemistry, University of Zagreb, *Zagreb*, Jugoslawien, Ul. Soc. Rev. 8.

[1] M. Pušelj and Z. Ban, Croat. Chem. Acta **41**, 79 [1969].

[2] E. Zintl and F. Husemann, Z. Physik. Chem. Leipzig (B) **21**, 138 [1933].

[3] I. Pietrokowsky, Trans. AIME **200**, 219 [1954].