Acta Cryst. (1962). **15**, 531

The Intermetallic Phases in the Cobalt-Tantalum System

By R. D. Dragsdorf*

Department of Physics, Kansas State University, Manhattan, Kansas, U.S.A.

and W. D. Forgeng

Metals Research Laboratories, Union Carbide Metals Company, Division of Union Carbide Corporation, Niagara Falls, New York, U.S.A.

(*Received* 28 *March* 1960 *and in revised form* 10 *August* 1961)

An X-ray diffraction study of cobalt–tantalum alloys containing 5, 10, 15, 35, and 60·6% tantalum by weight has been undertaken. Two new phases are reported: a metastable ordered phase of the Cu_3Au type, α-Co_3Ta, $a = 3{\cdot}647 \pm 0{\cdot}004$ Å; and a four-layered phase resembling the hexagonal Laves $MgNi_2$-type but with twice the a-axis periodicity. The presence of the three-layered cubic, $MgCu_2$-type, and four-layered, $MgNi_2$-type, hexagonal Laves phases has been confirmed. The existence of a third Laves phase, α-Co_2Ta, of the two-layered hexagonal $MgZn_2$-type with

$$a = 4{\cdot}797 \pm 0{\cdot}006 \text{ Å} \quad \text{and} \quad c = 7{\cdot}827 \pm 0{\cdot}010 \text{ Å}$$

has been established. The interrelationships among the various intermetallic phases in the cobalt–tantalum system are discussed.

Introduction

Previous investigations of the equilibrium phases of the cobalt–tantalum system have been made (Hashimoto, 1937; Koster & Mulfinger, 1938; Wallbaum, 1941; Kuo, 1953; Elliot, 1954, 1956). Besides the α and β solid-solution regions in the cobalt-rich side of the equilibrium diagram, Wallbaum observed two modifications of the AB_2-type Laves phases. He reported the existence of a three-layered, cubic Co_2Ta phase of the $MgCu_2$ type and a four-layered, hexagonal $Co_{2\cdot2}Ta_{0\cdot8}$ phase of the $MgNi_2$ type. Elliot reported that Co_2Ta was the cubic Laves phase from 600 to 1600 °C. He also found that the cobalt-rich $Co_{2\cdot19}Ta_{0\cdot81}$ was predominantly the cubic $MgCu_2$-type phase at 800 °C., a mixture of cubic and the two-layered, hexagonal $MgZn_2$-type phase at 1000 °C., only the $MgZn_2$-type structure at 1200 °C., and only the $MgCu_2$-type phase at 1400 °C. Clearly a discrepancy existed in the designation of the structure of the polymorphic forms. In addition, the unit cell dimensions for the cubic phase reported by the two workers differ by 0·4%. The $MgZn_2$-type phase has been observed by Elliot but its lattice parameters have not been reported. While Wallbaum & Elliot agree that Co_2Ta is the cubic Laves phase, they disagree completely on the slightly richer cobalt alloys.

The present investigation was undertaken to clarify the cobalt–tantalum equilibrium structures on the cobalt-rich side of the phase diagram, to determine the unit-cell dimensions of the known phase as well as those of two previously unreported phases, and to formulate the kinetics for the formation of the three Laves phases with nearly the same atom composition.

Procedure

The binary cobalt–tantalum alloys were prepared by vacuum melting using cobalt rondelles and technically pure tantalum sheet as raw materials. Samples of 5, 10, 15, 35, and 60·6% tantalum by weight were prepared and studied either in the as-cast condition or after periods of isothermal aging at temperatures from 700 to 1250 °C. for times ranging from 15 min. to 1000 hr. Prior to aging, some of the samples were given a solution treatment which consisted of holding the alloys at 1250 °C. for 2 hr. Further details on changes in microstructure, hardness, and electrical resistivity of these alloys as a result of heat-treatment have been reported (Korchynsky & Fountain, 1959).

X-ray powder diffraction patterns have been made of the alloys after a variety of heat-treatments. Cobalt $K\alpha$-radiation, $\lambda = 1{\cdot}7902$ Å, was utilized on samples which had been reduced to powder by grinding the alloys with a high-speed Alundum wheel. Since it was found that the intermetallic compounds could be isolated as a residue by preferentially dissolving the matrix material of the ground particles in a 10% HCl aqueous solution, this method was also employed for some samples.

Fig. 1 is the modified cobalt–tantalum equilibrium phase diagram resulting from the X-ray diffraction study reported here and from the metallographic study reported elsewhere (Korchynsky & Fountain,

---

* This work was done while R. D. Dragsdorf was at the Metals Research Laboratories, Union Carbide Metals Company, Division of Union Carbide Corporation, Niagara Falls, New York, on leave from Kansas State University.

Table 1. *Intermetallic compounds identified in the binary cobalt–tantalum system*

Phase	Nominal % Ta	Description of structure	Unit-cell dimensions	Molecules per unit cell	Calculated density (g.cm.$^{-3}$)	Reference
α-Co_2Ta	60·5	Hexagonal, two-layered Laves phase, $MgZn_2$ type	$a =$ 4·797 ± 0·006 Å $c =$ 7·827 ± 0·010 Å $c/a =$ 1·632	4	12·73 ± 0·048	Present authors
β-Co_2Ta	60·5	Cubic, three-layered Laves phase, $MgCu_2$ type	$a =$ 6·733 – 6·719 ± 0·006 Å	8	(13·01 – 13·09) ± 0·035	Wallbaum
			$a =$ 6·759 Å	8	12·86	Elliot
			$a =$ 6·778 ± 0·014 Å	8	12·75 ± 0·079	Present authors
γ-Co_2Ta ($Co_{2\cdot2}Ta_{0\cdot8}$)	52·7	Hexagonal, four-layered Laves phase, $MgNi_2$ type	$a =$ 4·732 ± 0·01 Å $c =$ 15·42 ± 0·01 Å $c/a =$ 3·26	8	12·19 ± 0·059	Wallbaum
			$a =$ 4·700 ± 0·017 Å $c =$ 15·42 ± 0·074 Å $c/a =$ 3·281	8	12·36 ± 0·15	Present authors
α-Co_3Ta	50·6	Ordered cubic phase, Cu_3Au type	$a =$ 3·647 ± 0·004 Å	1	12·25 ± 0·04	Present authors
β-Co_3Ta ($Co_{2\cdot25}Ta_{0\cdot75}$)	50·6	Hexagonal, four-layered	$a =$ 9·411 ± 0·033 Å $c =$ 15·50 ± 0·057 Å $c/a =$ 1·647	24 (32)	11·99 ± 0·13	Present authors

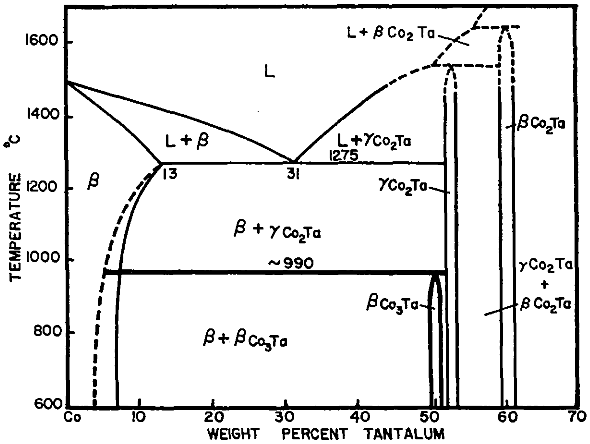

Fig. 1. The cobalt–tantalum equilibrium diagram. The heavy lines show a peritectoid reaction at about 990 °C.; the existence of a new phase, β-Co_3Ta; and a lower solubility of tantalum in cobalt.

Table 2. *Observed lattice spacings and observed and calculated intensities for the* α-Co_3Ta *phase*

hkl	*d* (Å)	Intensities Obs.	Intensities Calc.
100	3·616	*m*	37
110	2·563	*m*	31
111	2·092	*vs*	100
200	1·823	*w*	47
210	1·633	*vw*	16
211	1·491	*vw*	12
220	1·289	*m*	33
300	1·214	*vw*	2
310	1·150	*vw*	7
311	1·101	*m*	54
222	1·053	*w*	18
320	1·011	*vw*	8
321	0·9747	*w*	19

Ordered cubic structure, Cu_3Au type

$a = 3{\cdot}647 \pm 0{\cdot}004$ Å

Ta: 0, 0, 0

Co: 1/2, 1/2, 0;
1/2, 0, 1/2;
0, 1/2, 1/2.

$1 : \frac{\text{molecular unit}}{\text{unit cell}}$

1959). Table 1 gives a summary of the various intermetallic compounds identified in the range from 5 to 60% tantalum by weight.

X-ray diffraction patterns of the solution-treated samples of the 10 and 15% tantalum alloys showed only the face-centered cubic β-cobalt solid solution.* The lattice parameters of these cubic alloys were larger than those of pure β-cobalt because of the larger tantalum atoms. After aging these alloys at 800 °C. for 10 hr. or less, a metastable ordered phase α-Co_3Ta, of the Cu_3Au structure was observed. Further aging at this temperature caused the α-Co_3Ta phase to be replaced by a hexagonal, β-Co_3Ta phase. Lower temperature aging delayed the appearance of the metastable, α-Co_3Ta and its transition to β-Co_3Ta while higher temperatures (to 950 °C.) hastened the transitions. At 1000 °C., only the β-Co_3Ta phase was observed, and at 1100 °C., only γ-Co_2Ta ($Co_{2\cdot2}Ta_{0\cdot8}$), the $MgNi_2$-type phase, resulted. Table 2 shows the observed lattice spacings and line intensities for the α-Co_3Ta phase in comparison to the calculated intensities for the proposed ordered Cu_3Au structure. The relative intensities were calculated from the relation $m(\text{L.P.})F^2$ where m is the multiplicity, (L.P.) is the Lorentz-Polarization term, and F is the structure factor. The atomic scattering factors employed for these calculations were obtained from a compounded table (Peiser, Rooksby & Wilson, 1955). No attempt was made to correct for dispersion.

In the cast condition, the 35% tantalum alloy has a microstructure composed of eutectic plus the γ-Co_2Ta ($Co_{2\cdot2}Ta_{0\cdot8}$), $MgNi_2$-type phase. The γ-Co_2Ta phase persisted when the alloy was aged above

---

* Metallographic examination showed a small amount of a second phase in the 15% tantalum alloy.

Table 3. *Observed and calculated* $\sin^2\theta/\lambda^2$ *and intensity values for* α-Co_2Ta, $MgZn_2$-*type structure*

hkl	$\sin^2\theta/\lambda^2$ (obs.)	$\sin^2\theta/\lambda^2$ (calc.)	Intensity (obs.)	Intensity (calc.)	
10·0	0·01473	0·01448	*w*	17	
00·2	0·01659	0·01632	*w*	11	
10·1	0·01904	0·01857	*w*	15	
10·2	0·03129	0·03081	*w*	17	
11·0	0·04383	0·04345	*vs*	72	
10·3	0·05154	0·05121	*vs*	100	
20·0	0·05881	0·05794	*w*	16	
11·2	0·06035	0·05978	*vs*	94	
20·1	0·06248	0·06202	*s*	48	
00·4	0·06551	0·06530	*w*	5	
10·4	0·08052	0·07978	*w*	3	
20·3	0·09510	0·09467	*w*	6	
12·1	0·1056	0·1055	*w*	3	
10·5	0·1171	0·1165	*m*	13	
30·0	0·1303	0·1304	*m*	13	
12·3	0·1380	0·1381	*s*	41	
30·2	0·1468	0·1467	*s*	23	
20·5	0·1604	0·1600	*s*	30	
12·4	0·1666	0·1667	*w*	2	
22·0	0·1734	0·1738	*s*	24	
22·2	0·1905	0·1901	*m*	3	5
31·0		0·1883		1	
11·6		0·1904		1	
21·5	0·2035	0·2034	*vs*	16	43
31·2		0·2046		3	
20·6		0·2049		24	
10·7	0·2143	0·2145	*w*	4	
31·3	0·2246	0·2250	*vs*	33	
40·0	0·2326	0·2317	*vw*	3	
40·1	0·2346	0·2358	*m*	10	
22·4	0·2386	0·2391	*m*	7	
40·2	0·2480	0·2481	*vw*	1	
21·6	0·2487	0·2483	*s*	21	
31·4	0·2534	0·2536	*w*	2	
20·7	0·2592	0·2579	*vw*	0·1	
00·8	0·2624	0·2612	*vw*	1	
40·3	0·2674	0·2685	*w*	4	
32·0	0·2759	0·2752	*m*	2	15
10·8		0·2757		13	
31·5	0·2896	0·2903	*s*	23	
21·7	0·3012	0·3014	*m*	12	
41·0	0·3049	0·3042	*s*	4	32
11·8		0·3046		28	

Hexagonal structure: $a = 4{\cdot}797 \pm 0{\cdot}006$ Å
$c = 7{\cdot}827 \pm 0{\cdot}010$ Å

$$4: \frac{\text{molecular units}}{\text{unit cell}}$$

4 Ta: ±(1/3, 2/3, 1/16); ±(1/3, 2/3, 7/16) .

8 Co: 0, 0, 0; 0, 0, 1/2; ±(1/6, 1/3, 3/4); ±(1/3, 1/6, 1/4); ±(5/6, 1/6, 1/4) .

Table 4. *Observed and calculated* $\sin^2\theta/\lambda^2$ *and intensity values for* β-Co_2Ta, $MgCu_2$-*type structure*

hkl	$\sin^2\theta/\lambda^2$ (obs.)	$\sin^2\theta/\lambda^2$ (calc.)	Intensity (obs.)	Intensity (calc.)	
111	0·01708	0·01633	*m*	17	
200	—	—	—	0	
220	0·04456	0·04353	*vs*	56	
311	0·06076	0·05986	*vs*	76	
222	0·06656	0·06530	*m*	8	
400	—	—	—	1	
331	0·1041	0·1034	*w*	4	
420	—	—	—	0	
422	0·1315	0·1306	*s*	21	
333	0·1473	0·1469	*s*	6	25
511				19	
440	0·1743	0·1741	*s*	19	
531	0·1906	0·1905	*w*	5	
600	—	—	—	0	
442					
620	0·2173	0·2177	*m*	15	
533	0·2341	0·2340	*m*	16	
622	0·2392	0·2394	*w*	6	
444	0·2619	0·2612	*vw*	1	
711	0·2773	0·2775	*m*	4	8
551				4	
640	—	—	—	0	
642	0·3042	0·3047	*vs*	100	

Face-centered cubic structure: $a = 6{\cdot}778 \pm 0{\cdot}014$ Å

$$8: \frac{\text{molecular units}}{\text{unit cell}}$$

8 Ta: 0, 0, 0
1/4, 1/4, 1/4
16 Co: 5/8, 5/8, 5/8
7/8, 7/8, 5/8
7/8, 5/8, 7/8
5/8, 7/8, 7/8
+ the face-centered translations

1000 °C., while at temperatures below 1000 °C., this phase was replaced by β-Co_3Ta. In an alloy of a lower tantalum content, 15% by weight, the same temperature stability relationship exists between γ-Co_2Ta and β-Co_3Ta.

The microstructure of an as-cast 60·6% tantalum alloy was solid solution plus the α-Co_2Ta phase of the $MgZn_2$ type. Upon aging this alloy at 900 °C. for 258 hr., the diffraction pattern for the solid solution disappeared leaving only that of α-Co_2Ta. Aging at higher temperatures, 1100 and 1200 °C., transformed the α-Co_2Ta to the $MgCu_2$-type phase. Once formed, the three-layered Laves phase was retained even after further aging for as long as 256 hr. at 900 °C. and 100 hr. at 1000 °C. Data for the three Laves phases in this system are presented in Tables 3, 4, and 5. The reason for repeating the data on the previously reported Laves phases of the three- and four-layered type is twofold. There is some discrepancy between the cubic lattice parameter reported in the present investigation and that reported by Wallbaum or Elliot. Also, a close relationship can be shown to exist between the γ-Co_2Ta ($Co_{2{\cdot}2}Ta_{0{\cdot}8}$) and the new β-Co_3Ta ($Co_{2{\cdot}25}Ta_{0{\cdot}75}$) phase presented in Table 6.

Interpretation of results

The Laves-type structures would be expected in the cobalt–tantalum system since the approximate ratio of the individual diameters is 1·16 (Laves, 1956). That is, the occurrence of these structures is dependent on the relative sizes of the two constituent atoms. In addition, this atom combination is one of the few alloy systems in which all three Laves phases are found. Laves & Witte, 1936, have shown a relationship between structure and valency in their work on ternary magnesium alloys.

Table 5. *Observed and calculated* $\sin^2\theta/\lambda^2$ *and intensity values for* γ-Co$_2$Ta, (Co$_{2.2}$Ta$_{0.8}$), MgNi$_2$-*type structure*

hkl	$\sin^2\theta/\lambda^2$ (obs.)	$\sin^2\theta/\lambda^2$ (calc.)	Intensity (obs.)	Intensity (calc.)	
10·1	0·01615	0·01614	*w*		24
00·4	0·01723	0·01682	*w*		15
10·2	0·01930	0·01930	*vw*		15
10·5	0·03978	0·04137	*m*		36
11·0	0·04512	0·04527	*s*		95
10·6	0·05325	0·05295	*s*		100
20·1	0·06186	0·06141	*vs*	27	83 + β-Co
11·4		0·06209		56	
20·2	0·06427	0·06457	*m*		47
00·8	0·06738	0·06728	*w*		7
21·0	0·1058	0·1056	*vw*		1
21·2	0·1091	0·1098	*vw*		3
10·10	0·1207	0·1202	*vw*		14
21·5	0·1313	0·1319	*vw*		15
30·0	0·1346	0·1358	*w*		17
10·11	0·1427	0·1423	*m*	5	50
21·6		0·1435		45	
30·4	0·1516	0·1526	*m*		31
21·7	0·1562	0·1571	*vw*		1
20·10	0·1654	0·1655	*m*		30
22·0	0·1792	0·1811	*m*		33
20·11	0·1873	0·1876	*vw*		1
31·0	0·1960	0·1962	*vw*		1
21·10	0·2104	0·2108	*vw*		17
10·14	0·2204	0·2212	*vw*		4
21·11	0·2318	0·2328	*w*		8
40·0	0·2429	0·2414	*vw*		1
31·7	0·2460	0·2477	*vw*	1	12
22·8		0·2484		11	
10·15	0·2515	0·2516	*vw*		1

Hexagonal structure: $a = 4{\cdot}700 \pm 0{\cdot}017$ Å
$c = 15{\cdot}42 \pm 0{\cdot}074$ Å

$$8:\ \frac{\text{molecular units}}{\text{unit cell}}$$

8 Ta: ±(1/3, 2/3, 27/32); ±(2/3, 1/3, 11/32);
±(0, 0, 3/32); ±(0, 0, 19/32) .

16 Co: 1/2, 0, 0; 0, 1/2, 0; 1/2, 1/2, 0; 1/2, 0, 1/2; 0, 1/2, 1/2;
1/2, 1/2, 1/2; ±(1/6, 1/3, 1/4); ±(2/3, 5/6, 1/4);
±(1/6, 5/6, 1/4); ±(1/3, 2/3, 1/8); ±(2/3, 1/3, 5/8).

The stability of the observed MgNi$_2$-type slightly cobalt-rich structure which has the intermediate electron-atom ratio of the three Laves phases then suggests that the effective valency of this transition metal is positive. Specifically, for the four-layered γ-Co$_2$Ta, an electron-atom ratio of approximately 1·8 after the work of Laves & Witte (1936) could be assumed. If tantalum has a valency of +5, cobalt would have an effective valency of +0·64. This is not too different from the value of +0·72 obtained by Elliot (1956) who assumed a valency of +4 for titanium in a TiCo$_2$ alloy. Pauling (1938) showed that the saturation magnetization for cobalt at a temperature of absolute zero was 1·71 Bohr magnetons per atom. Hume-Rothery & Coles (1954) argue that cobalt, having normally nine electrons, would upon absorbing 1·71 electrons in a given atom fill the 3*d* shell and have an excess of 0·71 electrons per atom in the 4*s* state. At least then 0·71 electrons per atom would go into the Brillouin zones, the antithesis of the negative valency proposal of Greenfield & Beck (1954). It is possibly this 4*s* shell electron gain by cobalt alloyed with titanium or tantalum that Elliot (1956) and the present authors observe. Jones (1953) has given a theoretical justification for the possibility of a changeable valency of transition elements in different intermetallic systems. His arguments, however, do not explain the various valencies experimentally observed for cobalt. It appears, therefore, that a valence variation occurs which is not as yet well defined.

Table 6. *Observed intensity and observed and calculated* $\sin^2\theta/\lambda^2$ *values for* β-Co$_3$Ta (Co$_{2.25}$Ta$_{0.75}$)

hkl	$\sin^2\theta/\lambda^2$ (obs.)	$\sin^2\theta/\lambda^2$ (calc.)	Intensity (obs.)
10·0	0·003793	0·003764	*w*
10·3	0·01331	0·01313	*m*
20·0	0·01525	0·01505	*vw*
20·3	0·02368	0·02442	*m*
10·5	0·03037	0·02977	*m*
21·2		0·03051	
11·5	0·03731	0·03730	*s*
00·6		0·03745	
22·1	0·04682	0·04620	*vw*
30·4	0·05054	0·05052	*m*
00·7		0·05097	
31·1		0·04997	
20·6	0·05256	0·05250	*vw*
31·3	0·05699	0·05829	*vs*
40·0	0·06078	0·06022	*s*
00·8	0·06756	0·06657	*s*
10·9	0·08758	0·08802	*vw*
50·0	0·09421	0·09409	*m*
41·5	0·1051	0·1050	*w*
33·3	0·1119	0·1110	*w*
22·8		0·1117	
40·7		0·1112	
50·5	0·1207	0·1201	*w*
51·2		0·1208	
22·10	0·1491	0·1492	*s*
00·12		0·1498	
33·8	0·1683	0·1682	*m*
60·6	0·1728	0·1729	*vw*
52·5		0·1728	
10·13	0·1794	0·1796	*vw*
61·5	0·1881	0·1878	*w*
43·8	0·2058	0·2058	*s*
33·10		0·2056	
71·1	0·2162	0·2156	*w*
33·11	0·2268	0·2275	*m*
61·9	0·2458	0·2461	*vw*
54·4		0·2462	
11·15		0·2453	
44·9	0·2651	0·2649	*w*
43·11		0·2651	
61·10		0·2659	
71·7		0·2655	

Hexagonal structure: $a = 9{\cdot}411 \pm 0{\cdot}033$ Å
$c = 15{\cdot}50 \pm 0{\cdot}057$ Å

$$24:\ \frac{\text{molecular units}}{\text{unit cell}}$$

It could also be stated that in Co$_2$Ta the four-layered phase results because of the excess of cobalt atoms. Here then in γ-Co$_2$Ta (Co$_{2.2}$Ta$_{0.8}$), every fifth tantalum atom would be replaced by a cobalt atom without changing the Laves-type bonding. A four-layered or perhaps larger stacking fault periodicity might be expected with such a substitution.

With samples closer to the proper percentage of each atom for a true AB_2 compound, in our case 60·6% tantalum for Co_2Ta, a two-layered $MgZn_2$-type Laves phase freezes from the melt. This implies that either this α-Co_2Ta phase has a region of stability at very high temperatures or the composition is slightly non-stoichiometric so as to give the Laves phase with the higher electron-to-atom ratio. This two-layered phase persists after aging for as long as 258 hr. at 900 °C. However, upon aging a 1100 and 1200 °C., this structure is readily transformed to a stable $MgCu_2$-type, three-layered Laves structure with its lower electron-to-atom ratio. This is due to the greater mobility of the tantalum atoms at these higher temperatures.* Further aging the now three-layered alloy for 256 hr. at 900 °C. and then for 100 hr. at 1000 °C. caused no further change in the structure. The two-layered as-cast structure, although metastable, persists indefinitely at temperatures below 1000 °C. because the tantalum atoms at these temperatures are relativity immobile. The three-layered phase, however, formed at temperatures above 1000 °C. and being the stable phase is retained at all lower temperatures.

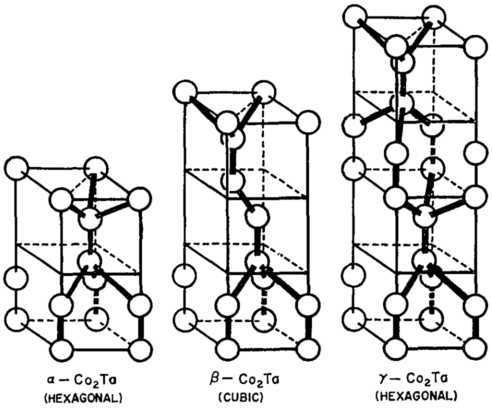

Fig. 2. The AB_2 laves phases showing only A (tantalum) atoms. The [111] cube direction is oriented in the [00·1] hexagonal directions for comparison.

Fig. 2 shows the relationship of the tantalum atoms in the two-, three-, and four-layered Laves phases. The cubic, three-layered phase, is drawn with the cube diagonal vertical for comparison with the hexagonal lattices. From this figure it becomes apparent why a periodic stacking fault can be visualized as the difference between the three phases.

Discussion

The β-Co_3Ta phase has been purposely omitted from consideration until the presence of the three Laves Phases was discussed. It is noted in Table 1 and 6 that this new phase is hexagonal and has approximately the same c-axis dimension as the four-layered Laves phase, γ-Co_2Ta. It has, however, just twice the a-axis dimension of both the hexagonal Laves phases making a cell volume which is four times the unit-cell size of the γ-Co_2Ta phase. It becomes apparent from Fig. 2 that a repositioning of the tantalum atoms in a new four-layered Laves-type lattice does not satisfy space requirements. Thus, if the four-layered system remains as seems most likely from the cell dimension, eight cobalt atoms in the γ-Co_2Ta would necessarily replace eight tantalum positions to form β-Co_3Ta in such a fashion that the periodicity obtained would be twice that previously observed in the directions perpendicular to the major axis.

It is to be noted that the β-Co_3Ta is closely related to the α-Co_3Ta ordered phase, in which the cobalt atoms have a coordination number of eight. α-Co_3Ta is a metastable phase which predetermines the cobalt atom orientation in the β-Co_3Ta equilibrium phase. In these alloys the α-Co_3Ta forms initially upon aging at temperatures under 1000 °C. and transforms to the β-Co_3Ta equilibrium phase. At higher temperatures, only the four-layered Laves phase exists. The similarity of the γ-Co_2Ta ($Co_{2\cdot2}Ta_{0\cdot8}$) phase to the β-Co_3Ta ($Co_{2\cdot25}Ta_{0\cdot75}$), phase might be made more striking by pointing out that the cobalt-rich γ-Co_2Ta phase may be considered as the substitution of one cobalt atom for every fifth tantalum atom, while the β-Co_3Ta could be thought of as the substitution of one cobalt for every fourth tantalum atom. The free energy difference between these two four-layered phases would be very small.

Berry & Raynor (1953) have shown that in cobalt–tantalum compounds the cobalt atoms appear closer together than in pure cobalt, while the tantalum atoms are farther apart than in pure tantalum. They have also shown that the distance between neighboring cobalt and tantalum atoms in the alloy is greater than the sum of the individual atomic radii of these atoms. The same results were found in this work for the Laves structures. However, as is shown in Table 7, the cobalt to tantalum distance in the non-equilibrium α-Co_3Ta phase was some 4·1% less rather than greater than the sum of the individual atomic radii. This ordered structure is coherent with the face-centered cubic cobalt matrix. The larger tantalum atoms give rise to a unit cell which is larger than that for pure

---

* The relationship $\tau = \nu \exp[-E/RT]$ is the probability that an atom of either cobalt or tantalum will move from one atom site to a vacant site per unit of time. ν is the jump frequency which is proportional to the temperature, E is the activation energy for this atom movement, and R is the molar gas constant. If the activation energy used in both cases was that for self-diffusion of each atom, it becomes apparent that above 900 °C. cobalt atoms move around quite easily in the lattice while tantalum atoms have a very low probability of movement until temperatures of 1100 to 1200 °C. are reached. This would explain why the as-cast $MgZn_2$-type phase is retained after lengthy periods of aging below 900 °C.

cobalt. The small cobalt–tantalum distance can be attributed to the tantalum valence electrons fitting into a vacant inner 3*d* shell of the cobalt atom.

Table 7. *Nearest neighbor distances in the observed* Co_2Ta *and* Co_3Ta *structures*

	Distances		
Structure	Co–Co	Ta–Ta	Co–Ta
Sum of the atomic radii of cobalt of coordination number six and tantalum of coordination number four	2·52 Å	2·86 Å	2·69 Å
α-Co_2Ta, $MgZn_2$ type	2·40	2·94	2·81
β-Co_2Ta, $MgCu_2$ type	2·40	2·94	2·81
γ-Co_2Ta, $MgNi_2$ type	2·35	2·89	2·77
α-Co_3Ta, Cu_3Au type	2·58	3·65	2·58

In conclusion, the agreement of the determined densities obtained in this work is emphasized. The α and β-Co_2Ta values are nearly identical while the γ-Co_2Ta ($Co_{2\cdot2}Ta_{0\cdot8}$) and Co_3Ta compounds are less dense in accord with their relative increases in cobalt. The interatomic distances presented in Table 7 agree extremely well for the Laves phases. These distances were calculated from the cell sizes determined in this work and reported in Table 1 and from the 'ideal' atom positions listed in the other tables. It is to be recognized that there are many possible faults in specifying the atom distances to the accuracy indicated in Table 7. However, it is felt that such a calculation, even using the 'ideal' atom positions in each case, helps corroborate the determined cell parameters.

The authors wish to acknowledge many stimulating discussions with M. Korchynsky and R. W. Fountain.

References

Berry, R. L. & Raynor, G. V. (1953). *Acta Cryst.* **6**, 178.

Elliot, R. P. (1954). *Armour Research Foundation, Chicago, Illinois, OSR Technical Note* OSR-TN-247, p. 22.

Elliot, R. P. (1956). *Armour Research Foundation, Chicago, Illinois Technical Report,* No. 1, File No. 20-6.

Greenfield, P. & Beck, P. A. (1954). *Trans. Amer. Inst. Min. (Metall.) Engrs.* **200**, 253, 759.

Hashimoto, U. (1937). *Nippon Kink. Gakk.*, **I**, 177.

Hume-Rothery, W. & Coles, B. R. (1954). *Adv. Phys.* **3**, 149.

Jones, H. (1953). *Phil. Mag.* **442**, 907.

Korchynsky, M. & Fountain, R. W. (1959). *Trans. Amer. Inst. Min. (Metall.) Engrs.* **215**, 1033.

Koster, W. & Mulfinger, W. (1938). *Z. Metallk.* **30**, 348.

Kuo, K. (1953). *Acta Met.* **1**, 720.

Laves, F. & Witte, H. (1936). *Metallwirtschaft*, **15**, 840.

Laves, F. (1956). *Theory of Alloy Phases*, pp. 124–198. American Society for Metals, Cleveland, Ohio.

Pauling, L. (1938). *Phys. Rev.* **54**, 899.

Peiser, H. S., Rooksby, H. P. & Wilson, A. J. C. (1955). *X-Ray Diffraction by Polycrystalline Materials*, pp. 656–659. London: The Institute of Physics.

Wallbaum, H. J. (1941). *Z. Kristallogr.* **103**, 391.

Wallbaum, H. J. (1941). *Arch. Eisenhüttenw.* **14**, 521.

Acta Cryst. (1962). **15**, 536

Nuclear Magnetic Resonance in Sodium Thiosulfate Pentahydrate*

By C. R. K. Murty and Z. M. El Saffar

Department of Physics, Michigan State University, East Lansing, Michigan, U.S.A.

(*Received* 10 *August* 1961)

The proton resonance spectrum of sodium thiosulfate pentahydrate has been studied with a view to establishing orientation of the water molecules. The orientation of the experimentally determined proton–proton vectors is in excellent agreement with those implied by the hydrogen bonding scheme suggested by Taylor & Beevers. One of the proton–proton vectors appears to be much shorter than those reported in other crystalline hydrates.

Introduction

The classic experiment of Pake (1948) established the fact that nuclear magnetic resonance data combined with X-ray information is quite effective in determining the position of hydrogen atoms in a crystal. The technique has been extended by latter workers to a number of simple hydrates i.e. hydrates with only a few pairs of *p–p* (proton–proton) directions. When one attempts to apply the method to more complicated hydrates one finds that the central portion of the proton resonance line is formed from the overlap of many components which are only partially resolved. Nevertheless at certain orientations some of the components of the resonance pattern are well resolved. The present work was undertaken largely to try to answer the question as to whether the information available from such orientation is sufficient to locate the protons in a relatively complicated hydrate.

The X-ray studies of Taylor & Beevers (1952) give

---

* This work was supported by the Office of Naval Research and the Air Force Office of Scientific Research.