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The Crystal Structure of Stoichiometric $CoIn_3$

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The compound $CoIn_3$ prepared at 400 °C is stoichiometric. Its crystal structure has been determined by single-crystal X-ray analysis. $CoIn_3$ crystallizes in the tetragonal system, space group $P4/mbm$. The unit cell, which contains eight atoms, has the dimensions $a = 6{\cdot}830$ and $c = 3{\cdot}547$ Å. The structure was refined by the least-squares method, using the positional parameters and isotropic temperature parameters. The structure is based on layers of square-triangular nets and is related to $CoGa_3$ and Si_2U_3 in that it is a disordered variant of the former and a defect structure of the latter. Whereas the geometry of the known compounds with the Si_2U_3 structure is closely tied to the conditions of spherical packing, $CoGa_3$ and $CoIn_3$ are characterized by a short bond distance Co–Ga and Co–In.

Introduction

Until quite recently, the information on phases in the cobalt–indium binary system was sparse. Some clarification of the phase equilibria and the composition of the intermetallic compounds was provided by Schöbel & Stadelmaier (1970). In looking over the preliminary structural information that we had on $CoIn_3$, we detected a relationship to tetragonal $CoGa_3$ (Schubert, Lukas, Meissner & Bhan, 1959) suggesting that our unit cell was essentially that of tetragonal $CoGa_3$ with half the cell constant c. Since a unit cell to be obtained by merely cutting the cell of the $CoGa_3$ type in half in this manner did not appear compatible with the tetragonal lattice actually observed, we believed that a full structure determination would shed some light on this problem.

Sample preparation and chemical composition

$CoIn_3$ was formed by reacting solid cobalt (99·74 wt. % purity) with liquid indium (99·99 wt. % purity) for 200 h at 400 °C and quenching to room temperature. The reaction layer consisted of a single phase sandwiched between the cobalt and the solidified indium. Although the grains in the reaction layer were mostly columnar, equiaxed crystals suitable for X-ray work could be isolated by digesting the reaction layer in dilute HCl.

The chemical composition was determined by electron-probe analysis, using a Hitachi XMA-5 microprobe. The compound layer was analyzed against standards of elemental cobalt and indium. Corrections for atomic number, absorption, and fluorescence effects were made using a computer program developed by Colby (1968). The composition, averaged from six independent and separately corrected determinations, was $24{\cdot}9 \pm 1{\cdot}2$ at. % Co and $75{\cdot}1 \pm 1{\cdot}2$ at. % In. A microprobe line scan through the compound layer showed that its composition was uniform. Therefore the microprobe evidence supports the assumption of stoichiometric $CoIn_3$.

Experimental

Approximate cell constants were obtained from 001 and 110 rotation patterns (camera diameter 10 cm, filtered Co $K\alpha$ radiation). The final cell constants were measured with a Straumanis-type powder camera (diameter 114·59 mm) extrapolating to $\theta = 90°$ and using Co $K\alpha_1$, $\lambda = 1{\cdot}78892$ Å and Co $K\alpha_2$, $\lambda = 1{\cdot}79278$ Å. The single-crystal integrated intensities of 194 reflections were collected with a manually operated Picker four-circle diffractometer using crystal-monochrom-

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Table 1. *Final parameters of* $CoIn_3$ *(with e.s.d.'s)*

	Number	Position	$10^4X/a$	$10^4Y/a$	$10^4Z/c$	B (Å^2)
In(1)	4	4 (h)	3458 (4)	8458 (4)	5000 (0)	1·19 (3)
In(2)	2	2 (a)	0 (0)	0 (0)	0 (0)	1·21 (4)
Co	2 (random)	4 (g)	1499 (12)	6499 (12)	0 (0)	0·46 (7)

Population factor for position 4 (g): 0·500 (11)
Secondary extinction factor g times 10^6: 12·7 (9)

atized Mo $K\alpha$ radiation and employing the moving-crystal moving-counter method (2θ scan) with $0 < 2\theta \leq 65°$. The hkl contained in one half-octant in reciprocal space were included. Because the Bragg angle of the quartz monochromator crystal is small for Mo radiation, only the standard polarization correction was used. In addition to the Lorentz correction, the spherical absorption correction taken from *International Tables for X-ray Crystallography* (1967) was applied. This was justified by the approximately spherical shape of the crystal; the value of μR was 6·0 with transmission factors A ranging from 0·010 to 0·068. The tetragonal cell data are $a = 6·830 \pm 0·001$, $c = 3·547 \pm 0·002$ Å, $c/a = 0·5193$, $V = 165·5$ Å^3, $D_x = 8·09$ g cm^{-3}.

Structure determination

The indices of the observed reflections obeyed the condition $0kl$: $k = 2n$. Observed very weak reflections 053 and 072 were readily identified as double reflections, the former by intensity reversal of apparent α_1 and α_2 the latter by the absence of $\alpha_{1,2}$ splitting at $2\theta = 49·3°$. Neither of these are possible in a properly aligned diffractometer with the monochromator set to pass Mo $K\alpha_1$ and α_2, nor was anything comparable observed in other reflections. The centrosymmetric space group that satisfies the systematic extinctions is $P4/mbm$ (No. 127). 194 observed reflections were used to fix eight parameters (two positional, three isotropic temperature, one population factor, one scale factor and an extinction parameter) in the final refinement, or 24 data per parameter. The basic structure was readily deduced from the cell dimensions and the strong reflections. Minor modifications in the occupancy of the atomic sites were tested before proceeding with the last refinement leading to the parameters reported here. The structure calculations were carried out with the CRYM Crystallographic Computing System (Duchamp, 1964). The structure was refined by a full-matrix least-squares method in which the function minimized was $\sum w^2(|F_o|^2 - |1/k\,F_c|^2)^2$. A Hughes $1/F_o^2$ weighting scheme was used to provide the weights. A population factor was included in the refinement to verify the fractions of the fourfold cobalt position occupied by cobalt and vacancies. Visual inspection of the list of F_o and F_c after refinement of the positional and isotropic thermal parameters suggested the need for a secondary extinction correction, so this was included in the final refinement cycles. The program uses the expression of Larson (1967) for the extinction-corrected F_c^2, which is equal to $F_c^2/(1+\beta g F_c^2)$, and assumes negligible absorption.

Table 2. *Observed and calculated structure factors* ($\times 10$) *for* $CoIn_3$

h	1	0	5	327	-340	5	382	-387	2	736	728	h	3	3	h	3	4
			6	255	289	6	78	-62	3	89	-90						
1	153	150							4	886	899	1	114	83	1	686	700
			h	9	0	h	7	1				2	267	234	2	86	-76
h	2	0							h	5	2	3	840	833	3	373	-392
			1	550	532	1	593	588									
0	110	92	2	198	-189	2	392	366	1	399	354	h	4	3	h	4	4
1	682	747	3	269	-202	3	150	-66	2	550	525						
2	769	818	4	110	129	4	246	-226	3	503	470	0	810	735	0	314	-272
			5	262	245	5	320	335	4	369	-348	1	556	504	1	306	-230
h	3	0				6	116	-133	5	289	300	2	249	216	2	467	445
			h	10	0	7	377	417				3	162	141	3	60	-51
1	1134	1171							h	6	2	4	111	83	4	597	580
2	173	-177	0	352	-343	h	8	1							5	201	209
3	764	-768	1	116	-95				0	1172	1089	h	5	3			
			2	427	392	0	317	295	1	190	-175				h	5	4
h	4	0				1	714	-616	2	79	75	1	424	381			
			h	0	1	2	335	294	3	61	-35	2	788	-746	1	250	211
0	584	-557				3	186	-177	4	217	-219	3	234	223	2	338	311
1	513	-497	0	426	-362	4	253	254	5	136	154	4	488	470	3	303	289
2	818	867				5	545	589	6	622	718	5	243	264	4	201	-209
3	198	-111	h	1	1	6	195	204									
4	1009	1044							h	7	2	h	6	3	h	6	4
			1	944	883	h	9	1									
h	5	0							1	127	-102	0	105	-99	0	774	724
			h	2	1	1	78	83	2	225	-222	1	336	302	1	156	-101
1	476	435				2	412	407	3	839	885	2	417	423	2	49	41
2	639	633	0	980	916	3	494	490	4	157	144	3	92	87	3	70	-19
3	554	566	1	1059	-1053	4	252	-253	5	178	184	4	467	480			
4	421	-419	2	523	513				6	60	70	5	291	-290	h	0	5
5	347	358				h	10	1				6	49	-40			
			h	3	1				h	8	2				0	60	-94
h	6	0				0	502	476				h	7	3			
			1	162	134	1	110	90	0	376	371				h	1	5
0	1309	1236	2	388	361				1	314	317	1	455	422			
1	217	-213	3	1032	1114	h	0	2	2	224	223	2	278	267	1	327	323
2	117	92							3	70	70	3	49	-40	2	408	445
3	69	-43	h	4	1	0	1521	1408	4	152	156	4	160	-168	3	60	50
4	300	-257							5	264	-288						
5	187	185	0	1004	1010	h	1	2				h	8	3	h	2	5
6	820	827	1	692	729				h	9	2						
			2	345	324	1	116	100				0	221	219	0	325	339
h	7	0	3	217	206				1	487	461	1	493	-466	1	427	-445
			4	137	118	h	2	2	2	182	-158	2	245	215	2	185	170
1	228	-119							3	181	-178	3	148	-134	3	135	-128
2	282	-266	h	5	1	0	80	63									
3	986	1015				1	613	612	h	0	3	h	0	4			
4	190	171	1	558	550	2	662	680									
5	199	217	2	970	-1009				0	217	-210	0	1027	1088			
6	70	83	3	319	323	h	3	2									
7	250	-250	4	618	644				h	1	3	h	1	4			
			5	387	368	1	1093	1093									
h	8	0				2	151	-136	1	646	634	1	70	50			
			h	6	1	3	647	-636									
0	504	433							h	2	3	h	2	4			
1	377	376	0	152	-147	h	4	2									
2	309	262	1	424	423				0	661	657	0	61	30			
3	70	84	2	592	593	0	506	-448	1	770	-809	1	337	346			
4	245	185	3	131	119	1	431	-398	2	360	328	2	403	395			
			4	636	664												

Results

The absence of superstructure reflections in the 001 rotation pattern and the powder pattern preclude a cell constant c that is a multiple of the proposed 3·547 Å. The structure was refined to a final unweighted reliability index ($R = \sum|k|F_o| - |F_c||/\sum k|F_o|$ where k is the scale factor) of 0·062. The refined structural parameters and their e.s.d.'s (in parentheses) are listed in Table 1. Table 2 lists the observed and calculated structure factors. A projection of the structure down the c axis is shown in Fig. 1. The half-shaded cobalt atoms indicate that the fourfold cobalt position is occupied by two atoms at random. Fig. 1 is drawn using radii of 1·57 Å for indium and 1·25 Å for cobalt. Where the atomic distances are shorter than the sum of these radii, the bond appears compressed.

The interatomic distances calculated from the atomic parameters and the cell constants are found in Table 3, together with their e.s.d.'s.

Table 3. *Interatomic distances for* $CoIn_3$ (*with e.s.d.'s*)

Reference atom	Neighbor	Number of neighbors*	Distance
In(1)	Co	1*	2·593 (7)
	Co	2*	2·732 (7)
	In(1)	1	2·980 (1)
	In(2)	4	3·136 (3)
	In(1)	2	3·547 (2)
	In(1)	4	3·657 (1)
In(2)	Co	2*	2·601 (3)
	In(1)	8	3·316 (3)
	In(2)	2	3·547 (2)
Co	In(1)	4	2·593 (7)
	In(2)	2	2·601 (3)
	In(1)	2	2·732 (7)
	Co	½*	2·896 (2)
	Co	1*	3·547 (2)
	Co	2*	3·679 (2)

* For fully occupied Co site multiply by 2.

Discussion

The In(1) atoms in the $CoIn_3$ structure are arranged in stacks of square-triangular nets. In the most familiar structure based on square-triangular nets, the $CuAl_2$ type, the squares stack up to cubic antiprisms. In $CoIn_3$ they form cubes of In(1) atoms that are slightly compressed along the *c* axis of the unit cell (3·547 Å *vs.* 3·657 Å, see Table 3). The center of the cube is occupied by In(2) whose distance to its eight neighbors (3·136 Å) is about twice the conventional radius for metallic indium. Typical indium radii are: (*a*) from Pauling's (1960) single-bond radius adjusted for C.N. 8, 1·53 Å, (*b*) from the smallest atomic distance (C.N. 4) in elemental indium (*International Tables for X-ray Crystallography*, 1968) 1·63 Å, (*c*) from the atomic radii of Slater (1972) 1·55 Å. The formal description of $CoIn_3$, that ties it to related structures, can be given along the following lines: In(1) and In(2) form a skeleton that is also found in $CoGa_3$ (Schubert *et al.*, 1959), where it is occupied by gallium atoms, and in Si_2U_3 (Zachariasen, 1949) where it is occupied by uranium atoms. Then $CoIn_3$ has a defect Si_2U_3 structure with only half of the Si positions occupied. One could also say that the fourfold Co site in hypothetical Co_2In_3 is randomly occupied by two atoms. An alternative description is obtained by relating $CoIn_3$ to $CoGa_3$, which itself is a defect superstructure of the Si_3U_2 type produced by putting ordered vacancies into hypothetical Co_2Ga_3. This leads to a doubling of the *c* parameter. Then $CoIn_3$ is simply a degenerate variety of this $Co\square Ga_3$ structure type, obtained by disordering the cobalt atoms and the vacancies. This restores the original *c* parameter. The occupation of the small atom (Si or Co) sites in the three structures is illustrated in Fig. 2. Note that the cell of Zachariasen (1949) was shifted by $\frac{1}{2}\frac{1}{2}0$ and that of Schubert *et al.* (1959) was shifted by $c' = -\frac{1}{4}$ to make them both conform to our setting. The question of how the $CoIn_3$ cell can be half of the $CoGa_3$ cell is thus resolved in a simple way.

In a metallic structure geometrical arguments are often instructive, and an example of these applied to the $CuAl_2$ type is found in the work of Laves (1956). The Si_2U_3 structure can be derived from a body-centered cubic uranium structure by removing every other center atom and collapsing the empty cube into two adjoining trigonal prisms, each of which is filled with a silicon atom. For hard-sphere contact the following theoretical parameters are computed: space

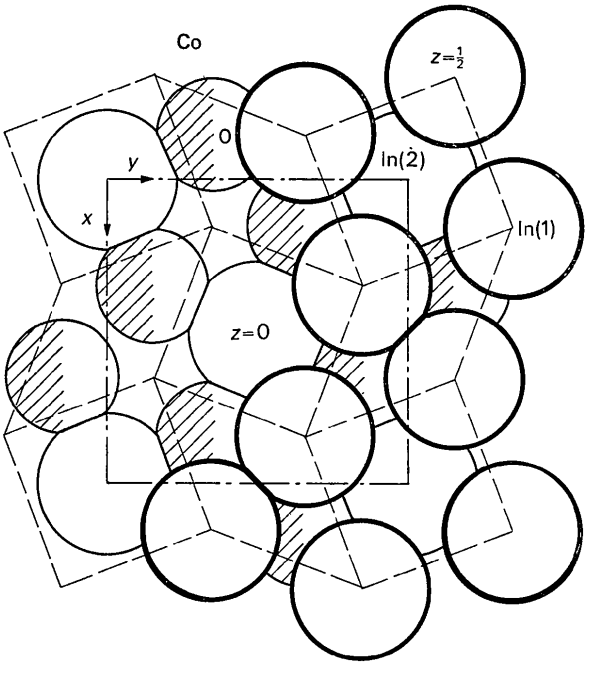

Fig. 1. Projection of $CoIn_3$ structure on to the *xy* plane. Some atoms are removed in the plane at $z=\frac{1}{2}$. Half-shaded circles indicate atoms with population factor ½.

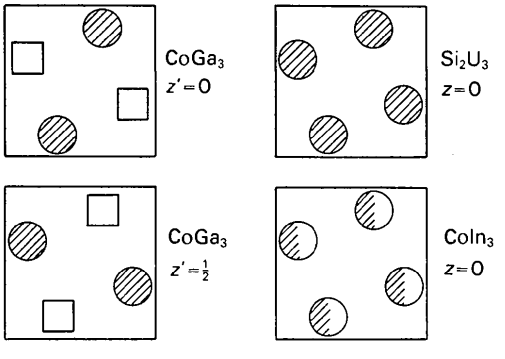

Fig. 2. Occupation of small-atom site in $CoIn_3$ and related structures. Squares indicate vacancies.

filling 0·64 (*vs.* 0·68 for b.c.c.), radius ratio U:Si 1·321, tetragonal c/a ratio 0·495, fractional positional parameters U, $x=0{\cdot}3117$; Si, $x=0{\cdot}1111$. In Zachariasen's (1949) setting the theoretical parameters are U, $x=0{\cdot}1883$; Si, $x=0{\cdot}3889$. The Si_2U_3 types for which the atomic positions are known, *i.e.*, Si_2U_3, Si_2Th_3, Al_2Th_3, Ga_2Ta_3, Ga_2Zr_3, Ge_2Th_3 (see Pearson, 1967), have x values that are quite close to the theoretical ones for spherical packing, but the defect types $CoGa_3$ and $CoIn_3$ are distorted noticeably. In them the effect of having $x>0{\cdot}3117$ is to rotate clockwise the cube of In(1) located in the center of the cell, Fig. 1. This shortens the In(1)–In(1) nearest-neighbor distance to 2·980 Å. It also decreases the cell constant a, and that is why the In(1) cube can appear compressed down the c axis while c/a still exceeds the theoretical 0·495. For cobalt, $x>0{\cdot}1111$, and consequently the cobalt nearest neighbors that touch in the rigid-sphere model, are separated to 2·896 Å (Table 2). Note that twice the C.N. 12 radius of cobalt is only 2·50 Å. Contrast this with the short Si–Si distance in Si_2U_3 which is observed to be 2·30 Å, a figure much smaller than the sum of the C.N. 12 radii (2·64 Å). The separation of the cobalt neighbors is accompanied by a contraction of the distance Co–In(1) to 2·593 or 2·601 Å. The sum of the C.N. 12 radii is 2·91 Å, the sum of the Slater (1972) radii is 2·90 Å. Better agreement is found with the sum of the Pauling (1960) radii assuming C.N. 6 for the cobalt atom to fix the bond number. The distance so derived is predicted to be 2·58 Å. The distortion against the rigid-sphere model is, then, attributable to a tendency of cobalt and indium to form a bond of that length.

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O.r.d. Studies of β-Amino Ketones. I. The Crystal Structure and Absolute Configuration of (+)-(1-Methyl-3-benzoyl-3-bromoacetoxypiperidine Hydrobromide)

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(+)-(1-Methyl-3-benzoyl-3-bromoacetoxypiperidine hydrobromide), $[(C_{15}H_{19}NO_3Br)^+Br^-]$ (IV) crystallizes in the orthorhombic space group $P2_12_12_1$. The lattice translations are $a=7{\cdot}200$ (3), $b=11{\cdot}312$ (4), $c=20{\cdot}776$ (7) Å. There are four molecules per unit cell; $D_x=1{\cdot}65$ and D_m ($HCCl_3$–$HCBr_3$) $=1{\cdot}64$ g cm^{-3}. The structure was determined by the heavy-atom method. Refinement of positional and thermal parameters by the block-diagonal, least-squares procedure converged at $R=0{\cdot}050$. The R-(+)-configuration was established from the anomalous scattering of the bromine atoms. The C(4)–C(3)–O(1)–C(7)–C(8) fragment is *trans–trans*. The benzoyl group is equatorial and the O(3)–C(9)–C(3)–C(2) torsion angle is 21·3°. Evidence is cited to support the predominance of the 21·3° rotamer in aqueous acid solutions of analogs configurationally related to IV by unequivocal chemical methods. Based on this conformation and configuration, optical rotatory dispersion data for analogs of IV in aqueous acid are consistent with antioctant behavior.

Introduction

Negative Cotton effects (Djerassi, 1960) have been reported for (+)-I and (−)-II in 0·1 N hydrochloric acid (Smissman & Hite, 1960), (Fig. 1). These compounds have the same configuration (Zalucky, Malspeis & Hite, 1964; Zalucky, Marathe, Malspeis & Hite, 1965; Patel & Hite, 1965*a*,*b*; Patel & Hite, 1967). Acetylation of (+)-I afforded (+)-III (Zalucky, Malspeis & Hite, 1964): m.p. 66–67°; $[\alpha]_D^{25}$ (ethanol) +34·7° (c 10·56); $[\alpha]_D^{25}$ (0·5 N HCl) +72·3° (c 11·14). R.D. (Fig. 1) in

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