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The Crystal Structure of La_3Co*

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The crystal structure of La_3Co has been determined by single crystal methods. There are four formula units in an orthorhombic cell, space group *Pnma*, with $a=7{\cdot}279$, $b=10{\cdot}088$ and $c=6{\cdot}578$ Å. The compound is isostructural with Al_3Ni and Fe_3C.

Introduction

Ternary alloys containing plutonium, lanthanum (or cerium) and iron, cobalt or nickel are of potential use as molten fuels in nuclear reactors. As part of a program of studying these ternary phase diagrams and their associated binary phase diagrams, the crystal structure of La_3Co has been determined.

Experimental

A stoichiometric mixture of La and Co was arc melted and then recast by vacuum induction heating in a Ta crucible. The alloy was slowly cooled to room temperature during a period of four hours. It was then crushed, and nearly all of the fragments were found to be single crystals. Preliminary examination of the crystals was made with a precession camera and Mo $K\alpha$ radiation. The crystals are not rapidly attacked by air, and a coating of Duco cement provided them with sufficient protection from oxidation. The unit cell was found to be orthorhombic. Systematic absences were $hk0$ with $h=2n+1$ and $0kl$ with $k+l=2n+1$. The space group, if centric, is therefore *Pnma*. The subsequent structural analysis showed this space group to be correct. Lattice constants were measured on the single crystal orienter with Mo X-rays ($K\alpha_1$, $\lambda=0{\cdot}70926$ Å) and found to be

$$a=7{\cdot}279,\ b=10{\cdot}088,\ c=6{\cdot}578\ \text{Å}$$

all $\pm 0{\cdot}005$ Å. The calculated density with four formula units per unit cell is 6·54 g.cm.$^{-3}$. The measured density was 6·48 g.cm.$^{-3}$.

It was possible to grind approximately spherical crystals of this compound. Such a sphere of $\mu R=2{\cdot}5$ was used in collecting intensity data with the single crystal orienter and Mo $K\alpha$ radiation. However, because the crystal was not a perfect sphere, and because of surface imperfections, the intensity of reflections when $\chi=90°$ varied somewhat with the angle φ. This variation was used in making an empirical absorption correction as a function of θ and φ. This correction was not large, its maximum value being 24%. In addition a spherical absorption correction was applied. Because it was anticipated that this would be a rather simple structure, without many parameters, an arbitrarily limited set of intensity data was collected. Reflections with $\theta_{Mo} \leq 20°$ were examined with the single crystal orienter and, of 249 non-extinguished reflections in this range, 232 were observed.

Determination of the structure

The space group was assumed to be *Pnma* and, because the $h0l$ and $h2l$ reflections are not similar in intensity, one La atom must occupy a general position. The other four La atoms and the four Co atoms were expected to be in fourfold sets $x, \frac{1}{4}, z$. A three-dimensional Patterson series was calculated and the approximate atomic positions were readily deduced.

A full-matrix, least-squares refinement with isotropic temperature factors was computed on an IBM 704. Form factors were employed in functional form by using the parameters given by Forsyth & Wells (1959). The final parameters are given in Table 1, and the observed and calculated structure factors are given in Table 2. The final value of R was 3·5%. The least-squares calculations were also made without applying the empirical absorption correction. For this case, R was 4·6% indicating that this absorption correction was at least a step in the right direction. Except for the scale factor, all parameter differences were considerably less than one standard deviation.

Discussion of the structure

The structure of La_3Co is similar to those of Al_3Ni (Bradley & Taylor, 1937) and Fe_3C (Lipson & Petch, 1940). The axial ratios and atomic parameters differ

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Table 1. *Final parameters in* La_3Co *from the least-squares refinement*

Atom	x	y	z	B (Å^2)
La_1	0·0461 ± 0·0003	¼	0·1434 ± 0·0004	1·63 ± 0·06
La_2	0·1688 ± 0·0002	0·0685 ± 0·0002	0·6727 ± 0·0002	1·55 ± 0·05
Co	0·3829 ± 0·0009	¼	−0·0604 ± 0·0010	2·20 ± 0·13

Table 2. *Observed and calculated structure factors for* La_3Co

If the observed value is negative the minus sign should be interpreted as 'less than'
The column headings are k, F_o, F_c

	$h=0$	$l=0$
2	63	−33
4	202	192
6	381	−408
8	52	−55

	$h=2$	$l=0$
0	46	−32
1	153	−152
2	278	−280
3	253	−255
4	160	156
5	209	−212
6	17	2
7	19	−8
8	168	179
9	71	82

	$h=4$	$l=0$
0	140	−128
1	13	−12
2	81	−78
3	317	321
4	23	16
5	74	72
6	77	75
7	96	96

	$h=6$	$l=0$
0	172	169
1	147	−137
2	149	150
3	110	108
4	53	−50
5	117	−119

	$h=0$	$l=1$
1	46	27
3	408	418
5	123	124
7	101	97
9	157	−161

	$h=1$	$l=1$
0	45	−37
1	33	−25
2	117	−110
3	214	217
4	60	58
5	33	34
6	−11	10
7	57	59
8	77	75
9	75	−83

	$h=2$	$l=1$
0	166	168
1	181	−186
2	278	273
3	46	−40
4	123	−119
5	186	−187
6	88	−84
7	60	55
8	184	−189
9	−13	−1

	$h=3$	$l=1$
0	263	252
1	132	−128
2	−10	−4
3	114	107
4	64	64
5	100	−97
6	157	−154
7	75	74
8	28	−26

	$h=4$	$l=1$
0	324	−315
1	109	−107
2	38	−37
3	49	−38
4	62	−58
5	122	−120
6	207	203
7	34	30

	$h=5$	$l=1$
0	19	−14
1	85	−84
2	91	−81
3	37	−34
4	52	46
5	105	−101
6	−13	6

	$h=6$	$l=1$
0	49	−47
1	78	79
2	70	67
3	151	145
4	56	−56

	$h=0$	$l=2$
0	197	−191
2	143	−145
4	40	37
6	113	106
8	103	107

	$h=1$	$l=2$
0	265	−273
1	255	−266
2	146	−147
3	60	59
4	28	20
5	241	−237
6	159	154
7	111	107
8	118	120
9	39	−47

	$h=2$	$l=2$
0	90	71
1	140	137
2	85	85
3	71	73
4	42	−34
5	152	151
6	42	−38
7	28	−28
8	64	−65

	$h=3$	$l=2$
0	62	−64
1	37	34
2	73	77
3	261	269
4	67	−64
5	108	104
6	51	48
7	69	63
8	53	−50

	$h=4$	$l=2$
0	23	16
1	20	−19
2	91	86
3	143	−142
4	52	−49
5	61	−59
6	17	−7
7	36	−33

	$h=5$	$l=2$
0	32	30
1	31	−29
2	206	207
3	105	−99
4	127	−123
5	62	−59
6	21	−7

	$h=6$	$l=2$
0	111	−107
1	−15	−0
2	62	−62
3	17	10
4	17	11

	$h=0$	$l=3$
1	22	−20
3	31	−25
5	33	−29
7	−12	4

	$h=1$	$l=3$
0	16	−4
1	93	−88
2	231	237
3	243	−248
4	147	−144
5	155	−153
6	21	17
7	34	−36
8	161	−163

	$h=2$	$l=3$
0	116	−115
1	40	−38
2	66	66
3	54	55
4	69	−68
5	29	−24
6	77	75
7	32	31
8	29	−31

	$h=3$	$l=3$
0	315	−316
1	73	74
2	101	−101
3	58	−56
4	25	−20
5	68	63
6	211	204
7	48	−47

	$h=4$	$l=3$
0	33	−29
1	58	−54
2	62	64
3	67	64
4	49	−48
5	43	−39
6	26	24

	$h=5$	$l=3$
0	115	111
1	160	161
2	65	66
3	51	57
4	17	−12
5	192	192

	$h=6$	$l=3$
0	−16	−10
1	−15	−10
2	−15	7

	$h=0$	$l=4$
0	211	−206
2	51	49
4	87	−84
6	138	140

	$h=1$	$l=4$
0	256	257
1	62	63
2	82	81
3	87	87
4	17	16
5	93	91
6	156	−164
7	−13	−3

	$h=2$	$l=4$
0	43	−43
1	93	91
2	117	114
3	−12	10
4	81	−83
5	97	99
6	37	37
7	37	−34

	$h=3$	$l=4$
0	70	64
1	28	−28
2	80	−74
3	227	−235
4	62	63
5	92	−95
6	45	−47

Table 2 (*cont.*)

	$h=4$	$l=4$
0	−15	−4
1	50	53
2	64	56
3	129	−133
4	43	−37
5	19	22

	$h=5$	$l=4$
0	112	−113
1	73	69
2	106	−107
3	46	52

	$h=0$	$l=5$
1	76	75
3	274	−276
5	−13	4

	$h=1$	$l=5$
0	80	−78
1	66	64
2	37	−32
3	92	93
4	−13	−1
5	88	95

	$h=2$	$l=5$
0	116	−113
1	114	117
2	101	−98
3	−13	−8
4	35	33
5	121	126

	$h=3$	$l=5$
0	101	103
1	23	21
2	92	96
3	23	−26
4	28	−33

	$h=4$	$l=5$
0	186	183
1	28	28
2	−16	6

	$h=0$	$l=6$
0	211	205
2	72	75

	$h=1$	$l=6$
0	−16	1
1	37	37
2	54	−55

	$h=2$	$l=6$
0	43	−43
1	101	−105

somewhat but are close enough so that the three compounds can be considered as isostructural. The axial ratios and atomic parameters for the three compounds are given for comparison in Table 3.

Table 3. *Atomic parameters and axial ratios of three A_3B compounds*

	La_3Co	Al_3Ni	Fe_3C
$x(A_1)$	0·046	0·011	0·040
$z(A_1)$	0·143	0·085	0·167
$x(A_2)$	0·069	0·174	0·183
$y(A_2)$	0·068	0·053	0·065
$z(A_2)$	0·672	0·644	0·667
$x(B)$	0·383	0·369	0·36
$z(B)$	−0·060	−0·055	−0·03
a/b	0·722	0·898	0·755
c/b	0·652	0·653	0·671

Table 4. *Interatomic distances in* La_3Co

The numerals in parentheses indicate the number of crystallographically equivalent distances. The standard deviations of La–La and La–Co distances are approximately 0·005 and 0·010 Å

	(Å)		(Å)		(Å)
Co–La_1	2·794	La_1–Co	2·794	La_2–Co	2·869
	2·988		2·988		2·978
	4·015		4·015		3·579
–La_2(2)	2·869	–La_1(2)	3·900	–La_1	3·707
(2)	2·978				3·773
(2)	3·579	–La_2(2)	3·707		3·830
		(2)	3·773		3·901
		(2)	3·830		4·034
		(2)	3·901	–La_2	3·620
		(2)	4·034		3·662
				(2)	3·758
				(2)	3·779

The structure of La_3Co in projection down the b axis is shown in Fig. 1. The interatomic distances are listed in Table 4. The atoms listed as neighbors are those that satisfy the definition given by Frank & Kasper (1958). The Co atom has nine La neighbors which form a convex polyhedron having 14 three-sided faces. Six neighbors form a distorted trigonal prism, and the other three neighbors are displaced outward from the rectangular faces of this prism. The La_1 atoms have three Co and 12 La neighbors. The convex polyhedron has 22 three-sided faces and two four-sided

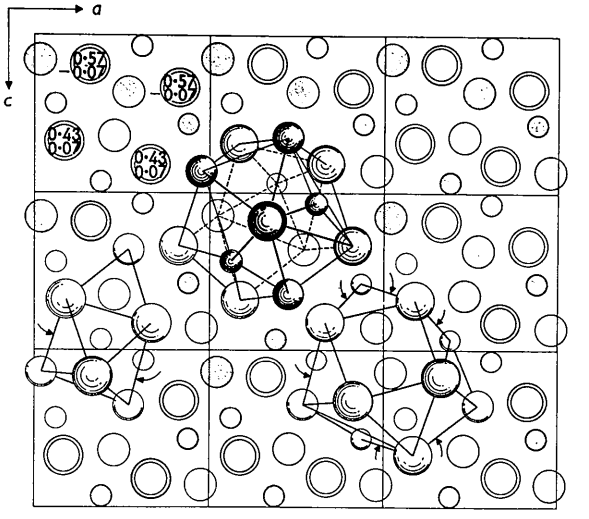

Fig. 1. The structure of La_3Co in projection down the b axis. The small circles are Co atoms, the large single circles are La_1 atoms and the large double circles are two superposed La_2 atoms. The shaded circles are at $y=\frac{1}{4}$, and the open circles are at $y=\frac{3}{4}$. The numbers in the upper left cell are the y coordinates of the La_2 atoms. The atoms making up the polyhedra are not shaded.

faces. In Fig. 1 the arrows indicate vertical three-sided faces bisected by the mirror at $y=\frac{1}{4}$. The La_2 atoms have three Co neighbors and 11 La neighbors which form a convex polyhedron having 20 three-sided faces and two four-sided faces. Edges of the convex polyhedra do not necessarily join neighbors in the Frank & Kasper sense, and, in some instances, lines joining neighbors are interior to the convex polyhedra.

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