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The Crystal Structure of Phase *C* in the Ternary System Cerium-Plutonium-Cobalt*

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Phase *C* in the ternary cerium–plutonium–cobalt system has the approximate formula $(Pu, Ce)_5Co_3$. The phase is tetragonal, space group *I4/mcm*, with $a = 10{\cdot}730$ and $c = 5{\cdot}383$ Å and is isostructural with W_5Si_3. A structure is proposed having vacancies, substitutional disorder and positional disorder.

Introduction

Molten cerium–plutonium–cobalt alloys are of potential use as fuel elements in nuclear reactors. This ternary phase diagram is currently being investigated by F. H. Ellinger, C. C. Land, K. A. Johnson and V. O. Struebing in this Laboratory. They have kindly supplied us with specimens suitable for single-crystal X-ray analysis. One of the ternary compounds, which has been designated phase *C* by Ellinger *et al.*, has the approximate formula $(Pu, Ce)_5Co_3$, although the amount of cobalt in the phase is about 37 at.% rather than 37·5 at.% as the above formula indicates. The cerium content of this phase ranges from 4 to 23 at.%. Structures of other ternary compounds in this system are being investigated and will be published as information becomes available.

Experimental

Two specimens of phase *C* having different cerium and plutonium contents were investigated by single-crystal techniques. These alloys were prepared by arc melting the components and then heat treating the resulting ingots. Pertinent information concerning these specimens is given in Table 1. The ingots were crushed and small single-crystal fragments were selected. Precession photographs showed phase *C* to be tetragonal, and the systematic absences, *hkl* if $h+k+l=2n+1$, $0kl$ if $l=2n+1$ and *hhl* if $l=2n+1$, showed that the space group is *I4/mcm* (if centric). Lattice constants were measured on a carefully aligned single-crystal orienter on a G. E. XRD5 using Mo radiation ($\lambda\, K\alpha_1 = 0{\cdot}70926$ Å). Both specimens had a small amount of $PuCo_2$ in addition to phase *C* as shown by photomicrographs. Thus, the amount of cobalt in phase *C* is a little less than 37·5 at.%.

Intensities for the complete hemisphere of a single crystal from each specimen were measured with the single-crystal orienter, Mo $K\alpha$ radiation and balanced filters. The maximum value of $2\theta_{Mo}$ was 50°. The shapes of the somewhat irregular fragments were defined as well as possible by a small number of bounding planes. Absorption corrections were computed by the Busing & Levy (1957) method using Burnham's (1962) program modified for single-crystal orienter geometry. *R* factors based on *F* and F^2 and formed by comparing the equivalent observed reflections (eight in number for general *hkl* reflections) with their mean values are given in Table 1. Absorption corrections were also made by applying empirical corrections based on the measured variation of intensity with φ at $\chi = 90°$, and applying spherical absorption corrections based on the average radius of the fragments. *R* factors of equivalent reflections were again computed. It is seen, in Table 1, that the agreement between equivalent reflections is much better with the empirical absorption corrections than with the formally more rigorous plane absorption calculations. The reason for this anomaly is the difficulty of measuring and defining the shape of a small irregular fragment.

Table 1. *Data concerning two specimens of phase C*

Specimen number		9222*B*	9223*A*
Gross composition	Ce	12·5 at.%	22·0 at.%
	Pu	50·0	40·5
	Co	37·5	37·5
Heat treatment		1000 hr, 400 °C	1000 hr, 400 °C +700 hr, 500 °C
a		10·730 ± 0·003 Å	10·743 ± 0·003 Å
c		5·383 ± 0·002	5·367 ± 0·002
Measured density		13·15 g.cm^{-3}	12·06 g.cm^{-3}
Number of non-equivalent reflections measured		170	170
Number of non-equivalent reflections observed		138	149
Plane absorption corrections			
R_F		10·1%	6·6%
R_{F^2}		19·9%	12·2%
φ and sphere absorption corrections			
R_F		6·7%	5·0%
R_{F^2}		12·0%	8·3%

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

Table 2. *Coefficients for analytic scattering factor curves*

Atom	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c	Maximum s
Co	13·695	5·824	6·090	0·813	3·194	54·998	—	—	3·987	1·50 Å^{-1}
Ce	21·465	2·758	19·761	0·223	12·127	16·287	2·794	128·200	1·832	1·99
Pu	36·576	0·497	23·790	3·223	16·679	14·156	3·405	93·209	13·513	1·99

Determination of the structure

All calculations were carried forward more or less simultaneously with the data from each of the two specimens. However, for brevity, the discussion from now on, unless otherwise stated, will apply to specimen 9222*B* and its data set with plane absorption corrections. The conclusions reached are the same regardless of which specimen or which data set is used.

The axial ratio, the approximate chemical formula and the probable space group suggested that the crystal has the $D8_m$ or W_5Si_3 structure (Aronsson, 1955*a*, *b*). A three-dimensional Patterson function was computed. This function was completely compatible with the $D8_m$ structure type. It is of interest that heretofore only metal silicides and germanides

Table 3. *Final isotropic parameters for* Pu_4CeCo_3

Atom	x	y	z	B
Pu	0·0862 ± 0·0006	0·2186 ± 0·0006	0	2·2 ± 0·2 Å^2
Ce	0	$\frac{1}{2}$	$\frac{1}{4}$	4·2 ± 0·5
Co(1)	0	0	$\frac{1}{4}$	2·1 ± 0·8
Co(2)	0·158 ± 0·002	$\frac{1}{2}+x$	0	2·2 ± 0·6

Table 4. *Final anisotropic parameters for* Pu_4CeCo_3

Atom	x	y	z	$B_{11}\times10^5$	$B_{22}\times10^5$	$B_{33}\times10^5$	$B_{12}\times10^5$
Pu	0·0860 ± 0·0004	0·2185 ± 0·0004	0	495 ± 41	375 ± 37	2665 ± 157	−52 ± 58
Ce	0	$\frac{1}{2}$	$\frac{1}{4}$	132 ± 67	B_{11}	16631 ± 1452	—
Co(1)	0	0	$\frac{1}{4}$	386 ± 151	B_{11}	756 ± 901	—
Co(2)	0·1576 ± 0·0013	$\frac{1}{2}+x$	0	264 ± 113	B_{11}	4915 ± 1156	215 ± 264

Table 5. *Observed and calculated structure factors for anisotropic ordered phase C*

The column headings are h, F_o and F_c. A minus sign preceding F_o means 'less than'

```
K=  0  L=  0

  2   -36   -57
  4   276   239
  6   213  -245
  8   -55    47
 10   331   346
 12   157   192

K=  0  L=  2

  0   834  1009
  2   440  -458
  4   177  -170
  6   513  -535
  8   213  -225
 10    94    87
 12   -65   -15

K=  0  L=  4

  0   650   720
  2    67   -89
  4    73    64
  6   187  -216
  8   -62   -32

K=  0  L=  6

  0   282   260
  2   121  -102
  4   -69   -21

K=  1  L=  0

  1   -32    43
  3   337  -297
  5   125   152
  7   551  -537
  9   224   236
 11   183  -200

K=  1  L=  1

  2   249  -254
  4   700  -693
  6   199   210
  8   184   194
 10   269   274
 12   118  -135

K=  1  L=  2

  1   139   143
  3   147  -147
  5   216   224

K=  1  L=  2

  7   365  -354
  9   270   290
 11    93   -86

K=  1  L=  3

  2   169  -186
  4   467  -461
  6   140   154
  8   131   129
 10   209   209

K=  1  L=  4

  1    78   127
  3   104   -65
  5   127   164
  7   239  -198
  9   178   188

K=  1  L=  5

  2   102  -111
  4   258  -235
  6    83    88

K=  1  L=  6

  1   -66     8
  3    87   -88

K=  2  L=  0

  2   154  -196
  4   791   738
  6   506   471
  8   313   299
 10    74    80
 12   111  -126

K=  2  L=  1

  3   642  -620
  5   274   270
  7   -49   -35
  9   -54     7
 11   179   198

K=  2  L=  2

  2   567  -563
  4   278   239
  6   113    88
  8   -57    -5

K=  2  L=  2

 10   129  -147

K=  2  L=  3

  3   429  -416
  5   178   172
  7   -55   -17
  9   -58    11
 11   134   141

K=  2  L=  4

  2   153  -171
  4   331   285
  6   209   190
  8   119   104

K=  2  L=  5

  3   248  -217
  5    96    80
  7   -65    -2

K=  2  L=  6

  2   167  -146

K=  3  L=  0

  3   275  -227
  5   126   145
  7   157   178
  9   174  -195
 11   161  -177

K=  3  L=  1

  4   -43   -28
  6   323   324
  8   512  -530
 10    72    84
 12   111  -116

K=  3  L=  2

  3    96   -72
  5   213   213
  7   226   236
  9    76   -70
 11    83   -67

K=  3  L=  3

  4   -51   -17

K=  3  L=  3

  6   237   234
  8   391  -392
 10    75    63

K=  3  L=  4

  3   -57     6
  5   128   149
  7   139   151
  9   -67   -29

K=  3  L=  5

  4   -59    -7
  6   141   130

K=  3  L=  6

  3   -70   -36

K=  4  L=  0

  4   -49   -54
  6   -50   -63
  8    90    92
 10   215   224
 12   267   278

K=  4  L=  1

  5   223   219
  7   145  -147
  9   182  -193
 11   -60    12

K=  4  L=  2

  4   382  -380
  6   328  -333
  8   153  -164
 10   -61   -12

K=  4  L=  3

  5   164   169
  7   113  -114
  9   139  -148

K=  4  L=  4

  4    89  -107
  6    77   -80
  8   -61    -5

K=  4  L=  5

  5    97   102

K=  5  L=  0

  5   714  -691
  7   -54   -17
  9   254  -252
 11   233   218

K=  5  L=  1

  6   172   182
  8   -57   -65
 10   190   205

K=  5  L=  2

  5   502  -487
  7   -59    79
  9   142  -130
 11   252   275

K=  5  L=  3

  6   129   127
  8   -61   -36
 10   148   150

K=  5  L=  4

  5   342  -288
  7   -62    62

K=  5  L=  5

  6    91    67

K=  6  L=  0

  6   520   507
  8   194   187
 10   -62   -53

K=  6  L=  1

  7   162   168
  9   214   229
 11   -65    15

K=  6  L=  2

  6   193   171
  8   -62   -57
 10   198  -226

K=  6  L=  3

  7   117   123
  9   164   170

K=  6  L=  4

  6   237   202

K=  7  L=  0

  7   306   283
  9   228  -232

K=  7  L=  1

  8   129   145
 10   131  -152

K=  7  L=  2

  7   330   339
  9   128  -118

K=  7  L=  3

  8   108   103

K=  7  L=  4

  7   224   233

K=  8  L=  0

  8   114   129

K=  8  L=  1

  9   160  -172

K=  8  L=  2

  8    80   -79

K=  9  L=  0

  9    79   -64
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Table 6. *'Apparent' thermal ellipsoids in phase C*

Atom	Axis	*B*	r.m.s. Amplitude	Orientation relative to the crystallographic axes *a*	*b*	*c*
Pu	1	2·3 ± 0·2 Å^2	0·171 ± 0·007 Å	11·8 ± 12·8°	101·8 ± 12·8°	90°
	2	1·7 ± 0·2	0·147 ± 0·007	78·2 ± 12·8	11·8 ± 12·8	90
	3	3·1 ± 0·2	0·197 ± 0·006	90	90	0
Ce	1	0·6 ± 0·3	0·088 ± 0·022	0	90	90
	2	0·6 ± 0·3	0·088 ± 0·022	90	0	90
	3	19·2 ± 1·7	0·493 ± 0·022	90	90	0
Co(1)	1	1·8 ± 0·7	0·15 ± 0·03	0	90	90
	2	1·8 ± 0·7	0·15 ± 0·03	90	0	90
	3	0·9 ± 1·0	0·11 ± 0·06	90	90	0
Co(2)	1	1·7 ± 0·9	0·15 ± 0·04	45	45	90
	2	0·7 ± 0·7	0·10 ± 0·05	135	45	90
	3	5·7 ± 1·3	0·27 ± 0·03	90	90	0

have been observed to have this structure. The ideal formula is thus Pu_4CeCo_3 with four formula units per unit cell and with the atoms in the following positions of $I4/mcm$:

Pu	in 16(*k*):	$x, y, 0$;	$x \sim 0{\cdot}09,\ y \sim 0{\cdot}22$
Ce	in 4(*b*):	$0, \frac{1}{2}, \frac{1}{4}$	
Co(1)	in 4(*a*):	$0, 0, \frac{1}{4}$	
Co(2)	in 8(*h*):	$x, \frac{1}{2}+x, 0$;	$x \sim 0{\cdot}16$.

The calculated density is thus 13·64 g.cm^{-3}, a rather high value as compared with the measured density of 13·15 g.cm^{-3}. This discrepancy will be discussed later.

A full-matrix least-squares refinement which minimized $\Sigma w(\Delta F)^2$ was then carried out. Observed reflections were given weights based on counting statistics according to the formula given by Evans (1961). Unobserved reflections were given zero weight. All *R* factors quoted include only observed reflections. The scattering factors were used in the analytic form

$$f(s) = \sum_{i=1}^{n} a_i \exp(-b_i s^2) + c\ ,$$

where $s = \sin\theta/\lambda$ and $n=3$ for cobalt and $n=4$ for cerium and plutonium. The coefficients are given in Table 2. Recently calculated relativistic scattering factors* for cerium and plutonium were used, and the scattering factor for cobalt was taken from *International Tables for X-ray Crystallography* (1962). Anomalous dispersion corrections, $\Delta f'$, of $-8{\cdot}26$, $-0{\cdot}38$ and $+0{\cdot}37$ electrons were applied to the plutonium, cerium and cobalt scattering factors, respectively.*

An isotropic refinement was first made leading to an *R* of 13·0% and giving the parameters in Table 3. These results appeared to be reasonable but it was noted that the thermal parameter of cerium was twice as large as that of any other atom. The final changes expressed as fractions of their standard deviations were all $<3\times10^{-6}$.

An anisotropic refinement was then computed and *R* was reduced to 7·5%. The final shifts expressed as fractions of their standard deviations were all $<4\times10^{-6}$. The anisotropic parameters are given in Table 4. A list of the observed structure factors and those calculated with the parameters of Table 4 is given in Table 5.†

Discussion of the structure and attempts at further refinement

The anisotropic thermal parameters were transformed to obtain the axes of the thermal ellipsoids and the

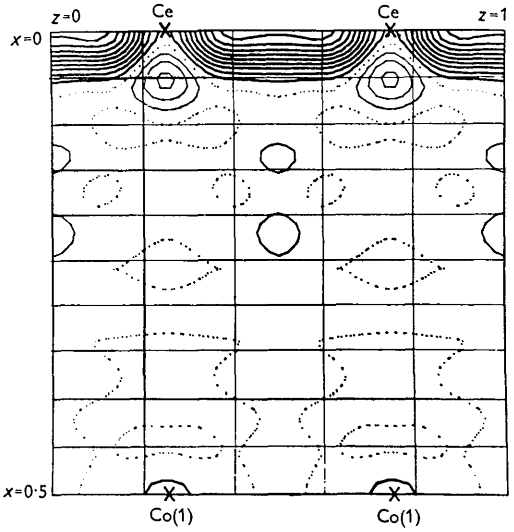

Fig. 1. Difference Fourier synthesis after isotropic refinement, $y=0{\cdot}5$ section. Contours are at 3 e.Å^{-3} intervals. The standard deviation of the electron density is estimated to be 3·4 e.Å^{-3}. Positive contours are heavy lines, negative contours light lines, and the zero contour is dotted.

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* Extensive tables of scattering factors and anomalous dispersion terms calculated from relativistic wave functions are in preparation.

† A similar list for specimen 9223*A*, with the higher cerium content, can be obtained from the authors.

orientation of the ellipsoids relative to the crystallorgaphic axes. The information is given in Table 6.

In attempting to interpret the above results, one must explain several things: (1) the phase is known to have a large composition range with respect to cerium and plutonium; (2) the ideal 37·5 at.% cobalt is never attained; (3) the measured density is appreciably lower than the calculated density of an ordered Pu_4CeCo_3 structure; (4) the extreme anisotropy of the 'apparent' thermal motion of the cerium and to a lesser extent that of Co(2) must be accounted for.

First let us note that the cerium in the set 4(*b*) leads to a linear chain of Ce atoms $c/2=2{\cdot}69$ Å apart. This is a Ce–Ce distance far shorter than in any other cerium intermetallic compound and it is thus unlikely that this set is fully occupied. Fig. 1 shows a difference Fourier section after the isotropic refinement. There is a large residual electron density along the line $0, \frac{1}{2}, z$. These peaks result from either a distribution of the cerium atoms about $z=\frac{1}{4}$ or a violent anisotropic thermal motion. The anisotropic temperature factor of the cerium leads to an r.m.s. amplitude of nearly 0·5 Å in the *z* direction, a value hardly compatible with the apparent 2·69 Å Ce–Ce distance along *z*. Fig. 2 shows a difference Fourier section after anisotropic refinement. There are still significant peaks midway between the cerium atoms. Fig. 3 shows an observed Fourier synthesis of this same section and it is seen that the electron density is quite smeared out along the line $0, \frac{1}{2}, z$.

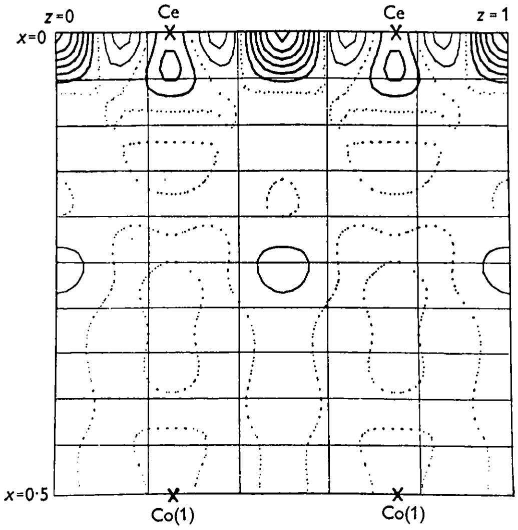

Fig. 2. Difference Fourier synthesis after anisotropic refinement, $y=0{\cdot}5$ section. Contours as in Fig. 1. The standard deviation of the electron density is estimated to be 1·9 e.Å^{-3}.

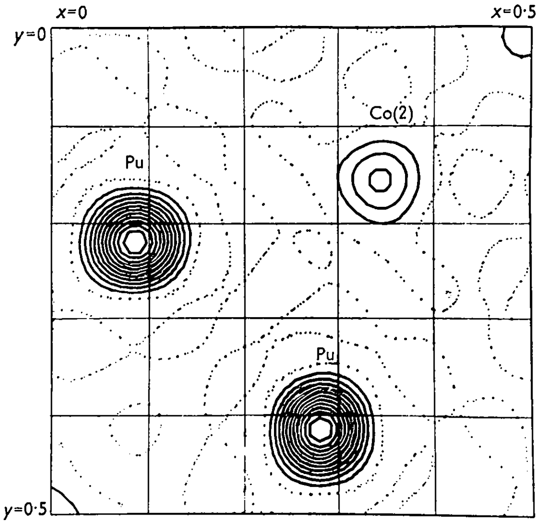

Fig. 4. Observed Fourier synthesis, $z=0$ section. Contours as in Fig. 3.

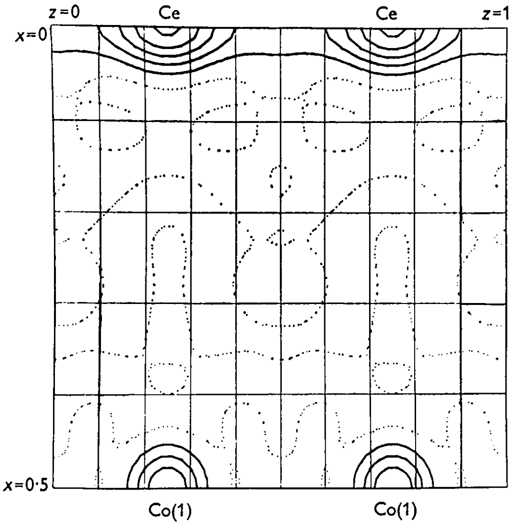

Fig. 3. Observed Fourier synthesis, $y=0{\cdot}5$ section. Contours are at 20 e.Å^{-3}.

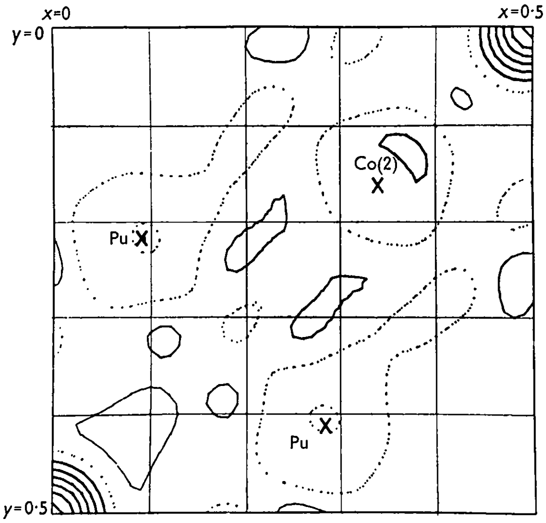

Fig. 5. Difference Fourier synthesis after anisotropic refinement, $z=0$ section. Contours as in Fig. 1.

Fig. 4 is an observed Fourier section at $z=0$ and Fig. 5 is a difference Fourier synthesis of this same section after anisotropic refinement. Nothing out of the ordinary is seen at the Pu or Co(2) positions.

We now propose the following type of disorder for specimen 9222*B*. The set 4(*b*) is only partially filled with cerium, and those atoms that are in this set are at $z=\frac{1}{4}$ only as an average or most probable value. One can think of starting with the ordered Pu_4CeCo_3 structure and removing cerium from set 4(*b*). For each cerium atom removed from the crystal, four plutonium atoms are also removed in order to retain the 4:1 Pu:Ce ratio. Then more cerium atoms leave set 4(*b*) and go into the 16-fold plutonium positions. Eventually enough cerium is removed so that the average Ce–Ce distance along the line $0, \frac{1}{2}, z$ is a reasonable value. As the cerium atoms get farther and farther from the $z=\frac{1}{4}$ location they begin to approach too closely to the Co(2) atoms in set 8(*h*). The Co(2) atoms then are pushed away in the *z* direction. The rather large apparent thermal motion of Co(2) in the *z* direction (Table 6), we therefore suggest, is a statistical variation of *z* coordinate about $z=0$ rather than thermal motion. Eventually the cerium atom approaches $z=0$ so closely that the Co(2) atoms cannot be pushed far enough away without becoming too close to other atoms and therefore are missing entirely. In this situation the most energetically favorable position for cerium is at $z=0$ rather than close to zero. Thus we have a slightly larger electron density at $0, \frac{1}{2}, 0$ in the observed Fourier shown in Fig. 3 than at $0, \frac{1}{2}, z$ where *z* is small. Also, the quite significant peaks at $0, \frac{1}{2}, 0$ in the difference Fourier synthesis of Fig. 2 are explained.

In the above analysis the tacit assumption has been made that no plutonium is in the set 4(*b*). There is no good reason for assuming this. However, if plutonium could readily go into both positions, one might expect the phase to be stable without any cerium.

Specimen 9223*A*, with 22 at.% cerium, is explained in the same manner, the only difference being that set 16(*k*) has a greater fraction of cerium.

Numerous attempts to least-square with additional parameters giving the fraction of vacancies in set 4(*b*) and the cerium fraction in set 16(*k*) were made. These parameters were so highly correlated with the scale and temperature factors, and depended so strongly on the anomalous dispersion terms, the weighting scheme and the scattering factors that nothing conclusive could be determined.

It has been our experience that the measured densities of arc-melted ingots consisting of a single phase, or very nearly a single phase, are fairly close to the computed densities. If we accept the measured value of 13·15 g.cm^{-3} as being correct, or only slightly low, we can compute, on the basis of the above model, how much cerium is missing in order to reduce the density to that which is observed. If we require that the cobalt content be 37 at.%, the Pu:Ce ratio be 4:1 and the density be 13·15 g.cm^{-3}, we arrive at the formula unit $P_{3\cdot867}Ce_{0\cdot967}Co_{2\cdot839}$. Let us rewrite this formula as $[Pu_{3\cdot867}Ce_{0\cdot133}]Ce_{0\cdot834}Co_{2\cdot839}$ where the brackets contain the atoms in the filled set 16(*k*). The average Ce–Ce distance in set 4(*b*) will now be 3·23 Å, which is a reasonable value.

The thermal anisotropy of the atoms in set 16(*k*) may be real but more likely is artificial. The two kinds of atoms in this set may occupy slightly different positions or these atoms may also be pushed aside by the cerium atoms in set 4(*b*) approaching $z=0$. In the recently determined structure of Pu_5Si_3 (Cromer, Larson & Roof, 1964), a well ordered representative of this structure type, the thermal motion of the plutonium in set 16(*k*) is essentially spherical.

The interatomic distances are given in Table 7. These have been computed from the parameters listed in Table 4 for an ordered Pu_4CeCo_3 crystal. Correlation terms and lattice constant errors have been included in the standard deviations. All distances involving cerium are of course without real meaning.

Table 7. *Interatomic distances in ordered phase C*

Pu–1 Pu	2·969 ± 0·008 Å	Co(1)–2 Co(1)	2·685 ± 0·001 Å
–2 Pu	3·260 ± 0·004	–8 Pu	2·857 ± 0·004
–2 Pu	3·355 ± 0·005		
–2 Pu	3·567 ± 0·006	Co(2)–2 Co(2)	3·885 ± 0·029
–2 Ce	3·435 ± 0·004	–2 Ce	2·744 ± 0·017
–2 Co(1)	2·857 ± 0·004	–2 Pu	2·830 ± 0·018
–1 Co(2)	2·830 ± 0·018	–2 Pu	2·936 ± 0·007
–1 Co(2)	2·936 ± 0·007	–4 Pu	3·094 ± 0·004
–2 Co(2)	3·094 ± 0·004		
Ce–4 Co(2)	2·744 ± 0·017		
–2 Ce	2·685 ± 0·001		
–8 Pu	3·435 ± 0·004		

All calculations were made on an IBM 7094 computer with programs written by the authors. The Fourier figures were made by an SC–4020 cathode ray plotter using input tapes prepared on the IBM 7094 computer.

We wish to thank F. H. Ellinger for many helpful discussions and V. O. Struebing for the preparation of the specimens.

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