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**The crystal structure of Pu<sub>3</sub>Co.\*** By ALLEN C. LARSON, DON T. CROMER and R. B. ROOF, Jr., *University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.*

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A Pu-Co alloy ingot of nominal composition 25.5 at.% Co was prepared by arc melting and then was heat treated at 440 °C for one week. It was not possible to obtain good quality single crystals because the fragments of the ingot became somewhat distorted when it was crushed. Nevertheless, after considerable searching, a crystal of poor but usable quality was found. After preliminary precession photographs had been taken, lattice constants and intensities were measured with a General Electric Co. XRD-5 equipped with a single-crystal orienter and scintillation counter. Crystallographic data are summarized in Table 1. The lattice constants are slightly larger than those found by Elliot & Larson (1957).

Table 1. *Crystallographic data for Pu<sub>3</sub>Co*

Orthorhombic, space group <i>Cmcm</i>	
$Z = 4$	
$a = 3.475 \pm 0.004 \text{ \AA}$	( $\lambda \text{ Mo K}\alpha_1 = 0.70926 \text{ \AA}$ )
$b = 10.976 \pm 0.010$	
$c = 9.220 \pm 0.008$	
$d_o = 14.82 \text{ g.cm}^{-3}$	
$d_c = 14.65 \text{ g.cm}^{-3}$	

Intensity measurements were made of reflections occurring at  $2\theta_{\text{Mo}} \leq 46^\circ$ , and most of the equivalent reflections were measured four times. After application of a spherical absorption correction based on the mean radius of the irregularly shaped fragment ( $\mu R = 3.4$ ), a  $\varphi$  correction based on the variation of intensity with  $\varphi$  for reflections at  $\chi = 90^\circ$ , and  $Lp$  corrections, the equivalent  $F_o^2(hkl)$  were averaged. The agreement between equivalent reflections expressed as  $\Sigma |F_H^2 - \bar{F}_H^2| / \Sigma F_H^2$  was 18%. Of 156 non-equivalent reflections, 119 were observed.

The structure was solved by packing considerations alone and this trial structure was later shown to be in agreement with the three-dimensional Patterson function. A least-squares refinement was then performed with the full matrix. All non-zero  $F_o$  were weighted equally. Form factors were used in functional form (Forsyth & Wells, 1959), and the parameters of Forsyth & Wells were used for Co. For Pu,

$$f_{\text{Pu}} = 45.91 \exp(-1.442 s^2) + 23.72 \exp(-15.32 s^2) + 7.13$$

where  $s = \sin \theta / \lambda$ .

Table 2. *Least-squares parameters for Pu<sub>3</sub>Co*

Atom	Set	$x$	$y$	$z$	$B$
Pu <sub>1</sub>	4c	0.0	$0.0778 \pm 0.0013$	$\frac{1}{4}$	$2.1 \pm 0.3 \text{ \AA}^2$
Pu <sub>2</sub>	8f	0.0	$0.3678 \pm 0.0009$	$0.0553 \pm 0.0010$	$2.2 \pm 0.2$
Co	4c	0.0	$0.778 \pm 0.005$	$\frac{1}{4}$	$3.7 \pm 1.2$

The above function is an excellent approximation to the Thomas-Fermi-Dirac Pu form factor curve (Ibers, 1960) with an anomalous dispersion correction of

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$\Delta f' = -16.5$  electrons (Roof, 1961). An anomalous dispersion correction of  $+0.4$  electron was applied to  $f_{\text{Co}}$ .

The final least-squares parameters are given in Table 2. The final observed and calculated structure factors, for which  $R = 15.9\%$  with  $F_o = 0$  omitted, can be obtained from the authors. Fig. 1 shows the asymmetric electron density section at  $x = 0$ . It is clear from the elliptic shapes

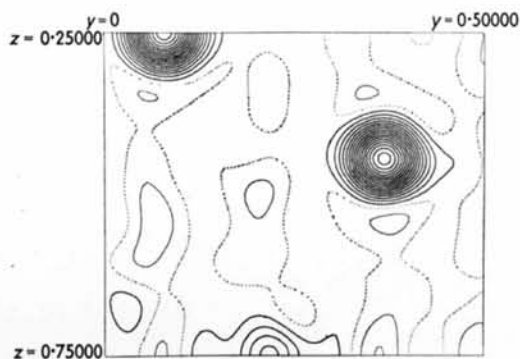


Fig. 1. Fourier sections of Pu<sub>3</sub>Co at  $x = 0$ . Contour interval is  $10 \text{ e.\AA}^{-3}$ . The zero contour is dotted. The light solid lines are negative.

of the peaks that anisotropic thermal parameters would improve the structure factor agreement. However, we believe that the quality of the intensity data is such that further refinement would be without value. Fig. 1 was drawn on 35 mm film by an SC 4020 high speed microfilm recorder. The Fourier synthesis was computed on an IBM 7090, and a 7090 program then was used to prepare a magnetic tape as the input to the SC 4020.

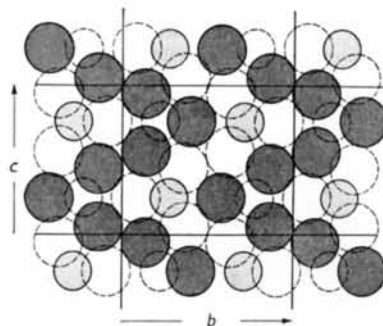


Fig. 2. Projection of Pu<sub>3</sub>Co as viewed down the  $a$  axis. The larger circles are Pu. The solid circles are at  $x = \frac{1}{4}$  and the dashed circles are at  $x = 0$ .

A projection of the structure as viewed down the  $a$  axis is shown in Fig. 2, and the interatomic distances are given in Table 3. Pu<sub>1</sub> has three Co and twelve Pu neighbors that form a convex polyhedron with 22 three-sided faces

Table 3. *Interatomic distances in Pu<sub>3</sub>Co.*  
*The standard deviation of Pu-Pu distances is 0.02 Å*  
*and for Pu-Co distances 0.06 Å*

Pu(1)-2 Pu(1)	3.48 Å	Pu(2)-2 Pu(1)	3.36 Å
Pu(1)-4 Pu(2)	3.36	Pu(2)-2 Pu(1)	3.40
Pu(1)-4 Pu(2)	3.40	Pu(2)-1 Pu(1)	3.65
Pu(1)-2 Pu(2)	3.65	Pu(2)-1 Pu(2)	3.08
Pu(1)-2 Co	2.80	Pu(2)-2 Pu(2)	3.28
Pu(1)-1 Co	3.29	Pu(2)-2 Pu(2)	3.48
		Pu(2)-1 Pu(2)	3.59
		Pu(2)-2 Co	2.69
		Pu(2)-1 Co	3.24
Co-2 Pu(1)	2.80		
Co-1 Pu(1)	3.29		
Co-4 Pu(2)	2.69		
Co-2 Pu(2)	3.24		
Co-2 Co	3.475		

and two four-sided faces. Pu<sub>2</sub> has three Co and eleven Pu neighbors that form a convex polyhedron with 16 three-sided faces and 4 four-sided faces. The Co atom has nine Pu neighbors, six of which form a trigonal prism and three of which are displaced outward from the four-sided faces of this prism. This is a common coordination for a relatively small atom surrounded by large atoms. In

this structure, however, there are two additional Co atoms that satisfy the Frank and Kasper (1958) definition of neighbor. These Co atoms are displaced by one unit cell in the *x* direction and lie outward from the ends of the trigonal prism.

Pu<sub>3</sub>Co is isostructural with the compound Al<sub>2</sub>CuMg (Perlitz and Westgren, 1943) and also with Re<sub>3</sub>B (Aronsson, Bäckman and Rundqvist, 1960).

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### Einige Strukturdaten zum Spinell 7ZnO.Sb<sub>2</sub>O<sub>5</sub>. Von H. SAALFELD, Lehrstuhl für Strukturforchung, Universität des Saarlandes, Deutschland

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Beim Erhitzen von ZnO und Sb<sub>2</sub>O<sub>3</sub> auf 1300 °C beobachtete Bayer (1961) die Bildung eines Spinells der Zusammensetzung 7ZnO.Sb<sub>2</sub>O<sub>5</sub> mit der Gitterkonstanten  $a = 8,585 \text{ \AA}$ . Für diesen Spinell schlug er die inverse Kationenverteilung Zn(Sb<sub>0,67</sub>Zn<sub>2,33</sub>)O<sub>4</sub> vor, ohne sie jedoch unter Beweis zu stellen. Kürzlich haben Linares & Mills (1962) Darstellungsmethoden zur Züchtung grosser ZnSb-Spinelle veröffentlicht. Aus Pulveraufnahmen ermittelten sie die Gitterkonstante  $a = 8,594 \pm 0,003 \text{ \AA}$ .

Die Beschäftigung mit Zn-Spinellen veranlasste den Verfasser, die Kationenverteilung des ZnSb-Spinells experimentell zu überprüfen. Durch 15-stündiges Erhitzen von ZnO und Sb<sub>2</sub>O<sub>3</sub> bei 1350 °C wurden genügend grosse Einkristalle erhalten. Guinier-Rückstrahlungen einer Pulverprobe ergaben eine Gitterkonstante von  $a = 8,594 \pm 0,001 \text{ \AA}$  in sehr guter Übereinstimmung mit den bisher ermittelten Werten.

Es wurden mit streng monochromatischer Mo-Strahlung Weissenbergaufnahmen der Zone [110] hergestellt und die Reflexe einzeln fotometriert und korrigiert (PL-Faktor, Absorption). Die erste Fouriersynthese lieferte neben der Kationenverteilung den Sauerstoffparameter. Mit weiteren Verfeinerungsrechnungen wurde ein R-Faktor von 0,10 erreicht. Hierbei ist ein isotroper Temperaturfaktor von 0,3 berücksichtigt worden. Es zeigte sich ferner, dass die starken Reflexe durch Primärestinktion geschwächt waren. Ein Vergleich mit Pulverauf-

nahmen ergab eine Schwächung der betroffenen  $F_o$ -Werte um etwa 15–20%.

Die Integration der Elektronendichten bestätigte die von Bayer vorgeschlagene Kationenverteilung. Die Tetraederlücken sind ausnahmslos durch Zn besetzt, während sich die restlichen Zn- sowie die Sb-Atome statistisch auf die Oktaederlücken verteilen.

#### Abstandsverhältnisse:

Sauerstoffparameter $x_0 = 0,239 \pm 0,001$	(Nullpunkt des Gitters im Zentrum)
	$0,386 \pm 0,001$ (Nullpunkt in $\frac{1}{3}m$ )
Zn-O :	2,02 Å (4-Koordination)
Zn-O }:	2,06 Å (6-Koordination)
Sb-O }	

Der Deutschen Forschungsgemeinschaft bin ich für die Bereitstellung von Röntgeneräten sehr zu Dank verpflichtet.

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