Oscillation, rotation, Weissenberg and precession X-ray photographs were taken about the needle axis, using Cu $K\alpha$ radiation. The unit cell was found to be monoclinic with the dimensions

$$a = 20 \cdot 73 \pm 0 \cdot 04, \quad b = 6 \cdot 34 \pm 0 \cdot 01, \quad c = 5 \cdot 20 \pm 0 \cdot 01 \text{ Å};$$
$$\beta = 93° \, 40' \pm 02'.$$

Complete examination of the zero, first and second layer photographs showed the following systematic absences:

> hkl reflections — only $h+k$ even present
> $h0l$ reflections — only l even present
> $0k0$ reflections — only k even present.

The three monoclinic space groups, C_s^3-Cm, C_2^3-C2 and C_{2h}^3-C2/m are consistent with the above X-ray data. On the other hand, the first and last possibilities, viz., Cm and $C2/m$ are ruled out, since the compound L-proline is asymmetric. Hence the space group is deduced to be C_2^3-C2.

The density of the compound was determined by the flotation method using benzene–bromoform mixtures. The observed density was $1 \cdot 324$ g.cm.$^{-3}$. On the basis

of the above unit cell, with four molecules per cell, the calculated densities for the free L-proline, the monohydrate and the dihydrate are $1 \cdot 129$, $1 \cdot 307$ and $1 \cdot 483$ g.cm.$^{-3}$ respectively. It will be seen that the observed density agrees best with the calculated value for the monohydrate. The slight discrepancy in the two values is to be attributed to the hygroscopic nature of the crystal, and the consequent error in the measurement. Thus the compound is identified to be L-proline monohydrate.

The point group could not be determined uniquely from morphological data, as complete data could not be obtained. The above space group assignment was however confirmed from the [001] Patterson projection which showed concentrations of peaks (Harker interactions) along $y = 0$ and $\frac{1}{2}$, as required by the space group.

The author wishes to express his sincere thanks to Prof. G. N. Ramachandran for his helpful guidance.

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The crystal structure of PuNi.* By DON T. CROMER and R. B. ROOF, JR., University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.

The Pu–Ni phase diagram published by Wensch & Whyte (1951) shows the existence of six binary compounds. The structures of $PuNi_2$, $PuNi_5$ and Pu_2Ni_{17} have been reported by Coffinberry & Ellinger (1956) and the $PuNi_3$ structure has been reported by Cromer & Olsen (1959). The structure of PuNi is the subject of the present note. The structure of $PuNi_4$, the remaining compound of the series, is currently being studied.

A Pu–Ni alloy containing 75 at.% Pu was heated to 1150 °C., well above the liquidus for that composition, and then thermally cycled between 445 and 475 °C. for about three months. Because PuNi is formed by a peritectic reaction, non-stoichiometric ratios of Pu and Ni were required in order to avoid the formation of the next higher Ni containing compound, $PuNi_2$. The specimen was crushed and fragments were examined with a precession camera. In spite of the prolonged heat treatment, good quality PuNi single crystals were impossible to find. Finally, however, one crystal of usable quality was found.

The crystal was found to be orthorhombic with

$$a = 3 \cdot 59 \pm 0 \cdot 01, \quad b = 10 \cdot 21 \pm 0 \cdot 02, \quad c = 4 \cdot 22 \pm 0 \cdot 01 \text{ Å},$$

as measured from precession photographs (Mo $K\alpha$, $\lambda = 0 \cdot 7107$ Å). The photographs showed the following systematic extinctions: hkl absent if $h+k = 2n+1$ and $h0l$ absent if $l = 2n+1$. These extinctions are characteristic of space groups $Cmcm$ or $Cmc2_1$. The space group and axial ratios suggested that the structure was of the TlI

type (space group $Cmcm$) and cursory examination of the intensities showed that this was indeed the case. In the TlI structure there are four formula units per unit cell with the larger atom (Pu in this case) in the set $4c$, with $y \approx 0 \cdot 14$, and the smaller atom in the same set with $y \approx 0 \cdot 42$. The calculated density of PuNi is thus $12 \cdot 9$ g.cm.$^{-3}$.

In order to define the y parameters more precisely, intensities of the $0kl$ zone were visually estimated from a precession photograph taken with Zr filtered Mo radiation. These intensities were corrected for the Lorentz-

Table 1. Observed and calculated $0kl$ structure factors for PuNi

k	l	F_o	F_c	k	l	F_o	F_c
0	2	287	−310	6	4	0	44
0	4	137	163	6	5	58	66
2	0	0	−11	8	0	91	80
2	1	237	−207	8	1	149	−147
2	2	0	13	8	2	81	−69
2	3	116	137	8	3	101	103
2	4	0	−12	8	4	40	48
2	5	69	−79	10	0	124	−108
4	0	277	−269	10	1	103	−84
4	1	186	168	10	2	101	93
4	2	203	207	10	3	83	61
4	3	112	−102	10	4	61	−64
4	4	93	−119	12	0	0	−11
4	5	38	51	12	1	104	84
6	0	72	70	12	2	0	11
6	1	162	171	12	3	74	−66
6	2	58	−62	14	0	106	83
6	3	108	−117				

polarization factors (Waser, 1951), but not corrected for absorption, and a least-squares refinement was computed on Maniac II. The scale factor, two isotropic temperature factors and the two y parameters were simultaneously refined. All terms of the normal equations were used. The Thomas–Fermi form-factor was used for Pu and the form-factor computed by Viervoll & Øgrim (1949) was used for Ni. Ten electrons were subtracted from the Pu form factor as an approximate correction for anomalous dispersion. The results of the refinement are

$$y_{Pu} = 0{\cdot}1421 \pm 0{\cdot}0009, \quad y_{Ni} = 0{\cdot}4221 \pm 0{\cdot}0034,$$
$$B_{Pu} = 1{\cdot}38 \pm 0{\cdot}21, \quad B_{Ni} = 2{\cdot}43 \pm 0{\cdot}81 \,.$$

The calculated and observed $0kl$ structure factors, for which $R = 10{\cdot}9\%$, are given in Table 1.

Each atom has seven neighbors of the opposite kind, four at $2{\cdot}85$, two at $2{\cdot}88$ and one at $2{\cdot}86$ Å. In addition, the Ni atom has two Ni neighbors at $2{\cdot}64$ Å and the Pu has eight Pu neighbors, two at $3{\cdot}54$ and six at $3{\cdot}59$ Å. The estimated standard deviations are $0{\cdot}02$ Å for Pu–Pu, $0{\cdot}04$ Å for Pu–Ni and $0{\cdot}05$ Å for Ni–Ni distances.

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A reply to some comments by Karle and Hauptman. By A. KLUG, *Birkbeck College Crystallography Laboratory, University of London, 21 Torrington Square, London, W. C.* 1, *England*

In a recent paper Karle & Hauptman (1959) comment, in a lengthy footnote, on a paper of mine (Klug, 1958) on the phase problem. They state that in a previous paper of theirs (Karle & Hauptman, 1956) they had already derived 'measures of statistical significance based on the appropriate variances' of individual terms in phase-determining formulae. I did not refer to this paper earlier since the relevant discussion in it on variances is concerned with two points, both of which had already been adequately dealt with in earlier papers by other workers, which I did cite. The first point, on the degree of validity of a formula according as the atoms in the cell are equal or not, has been discussed by Cochran (1954) and Cochran & Woolfson (1955), while the second, on the weighting of the terms in a formula by their variances, had first been discussed by Bullough & Cruickshank (1955). In any case it is misleading to claim that the discussion in Karle & Hauptman's (1956) paper yields 'measures of statistical significance' that throw any critical light on the whole problem. No explicit mention is made there of the dependence of the variances and hence of the reliability of the formulae on the number of atoms in the unit cell, which, together with the finite amount of data, sets the principal limitation to the use of statistical or algebraic methods. Nor were the calculations made to a high enough order of accuracy to show how the *variance* of the estimate of the sign of a structure factor depends on the magnitudes of the E's involved in the sign relation being studied (cf. expressions [3·20], [3·30], and [3·35] of my paper, and particularly [5·14] and the discussion following it). It is therefore not at all possible to study from Karle & Hauptman's calculations the effect of unusually large E values, on which the success of the formulae is expected to rest. Their newest approach (1959) suffers from the same defects so that it is not at all clear from it under what conditions the formulae given would be valid in practice.

These points, and others, were considered in my paper, in which measures of significance were given to phase-determining relations by introducing the concept of the order of a relation. My conclusion that only relations of the lowest order could be expected to be generally useful has been recently confirmed by Cochran (1958).

However, as Karle & Hauptman state, the most convincing test of any phase-determining theory is in its practical application to the solution of crystal structures. In view of the criticisms that have been made of their claim to have devised a *routine* procedure for solving the phase problem, valid whatever the number of atoms in the unit cell, it is to be hoped that failures, as well as successes, of the method will be recorded. Furthermore it would be generally very helpful to continue to assess (cf. Karle *et al.*, 1957), in the case of a successful application of the method to a structure of some complexity, which of the formulae played a key role in the solution, and also, if possible, to discuss the relation of these to other methods for solving crystal structures (cf. Wright (1958)).

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