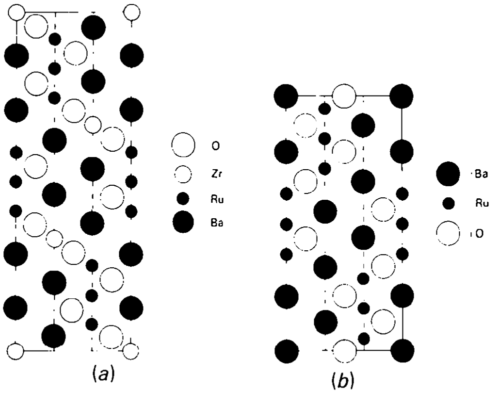

Fig. 2. (a) (110) plane of $Ba_4ZrRu_3O_{12}$ at 4·2 K. (b) (110) plane of $BaRuO_3$.

The 4·2 K neutron diffraction data give no indication of a three-dimensional ordering. The structures at both temperatures are essentially the same (Table 2); the Ru—Ru distances are nearly the same: 2·529 (6) Å at 300 K and 2·536 (7) Å at 4·2 K.

As already mentioned this type of structure is also found in $Ba_4MRu_3O_{12}$ (M = Nb, Ta) (Greatrix & Greenhouse, 1980), in $Ba_4Re_2M\square O_{12}$ (M = Mg, Cd, Co, Zn or Ca) (Longo, Katz & Ward, 1965) and in $Ba_4M_2W\square O_{12}$ (M = Nb, Ta) (Rother, Kemmler-Sack, Treiber & Cyris, 1980). In the last two cases the vacancies (□) are at the centre of the octahedra-string, between the (hh) BaO_3 layers.

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Structure (Neutron) of Room-Temperature Phase III Potassium Iodate, KIO_3

By B. W. Lucas

Department of Physics, University of Queensland, St. Lucia, Brisbane, Queensland 4067, *Australia*

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Abstract. M_r = 214·001, $P1$, a = 7·7436 (4), b = 7·7183 (4), c = 7·7328 (5) Å, α = 108·986 (4), β = 109·449 (4), γ = 109·209 (5)°, V = 359·12 (3) Å^3, Z = 4, D_m = 3·89, D_x = 3·96 g cm^{-3}, neutron powder diffraction (Rietveld method), λ = 1·9090 (1) Å, $F(000)$ = 320, T = 300 K, R = 7·50% for 716 integrated Bragg intensities. The triclinic structure proposed by Kalinin, Ilyukhin & Belov [*Dokl. Akad. Nauk SSSR* (1978), **239**, 590–593; *Sov. Phys. Dokl.* (1978), **23**, 166–168], from single-crystal X-ray diffraction, is confirmed, thereby resolving previous structural uncertainty.

Introduction. At atmospheric pressure, potassium iodate has been reported to undergo phase transitions with temperature change:

$$\begin{array}{ccccccccc} & 83\text{K} & & 255\text{ K} & & 343\text{ K} & & 485\text{ K} & \\ \text{V} & \rightarrow & \text{IV} & \underset{263\text{K}}{\rightleftarrows} & \text{III} & \rightarrow & \text{II} & \rightarrow & \text{I} \end{array}$$

and all phases, except I, are ferroelectric (Herlach, 1961). Attempts to determine the phase III crystal structure have been hindered by a tendency towards twinning and polymorphism, resulting in uncertainty of the true single-crystal nature of specimens used in the

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investigations (Náray-Szabó & Kálmán, 1961). Suggestions of pronounced pseudosymmetry have further added to the confusion and several differing crystal systems have been proposed (Smith & Welch, 1960; Herlach, 1961; Filimonov, Lomova, Suvorov, Pakhomov & Sonin, 1965; Crane, 1972).

In more recent years, two single-crystal X-ray structures have been proposed (Hamid, 1973; Kalinin, Ilyukhin & Belov, 1978) based on diffractometer data. However, these also show significant differences; the former structure has been criticized by Crane (1975) and Kalinin *et al.* (1978) for some questionable I—O interatomic distances.

The aim of the present investigation was to use the neutron powder profile method to resolve the structural uncertainty, since twinning and pseudosymmetry should be of less importance with this technique, the scattering powers of all atom types are more comparable, also absorption effects less, for neutrons than for X-rays.

Experimental. KIO_3 powder (of stated purity 99·9% minimum, obtained from May & Baker Laboratories, UK) was finely ground to fill a thin-walled vanadium sample can of 16 mm diameter. Atmospheric pressure and room temperature (300 K); high-resolution neutron powder diffractometer (*D1A*) at the high-flux reactor of the Institut Laue–Langevin (ILL) (Grenoble); *D1A* has a bank of ten ^{3}He high-pressure counters with a 6° angular separation. Resultant intensity profile obtained by appropriately combining the intensities from these counters to cover an effective 2θ range of 18·05 to 140·00° in 0·05° steps. Background under the diffraction peaks estimated by linear interpolation between points chosen in those regions devoid of reflections and subtracted from the total observed profile. No regions omitted within the 2θ scan. Scattering lengths: b_K = 3·7, b_I = 5·3 and b_O = 5·83 fm (Bacon, 1975; Schneider, 1976).

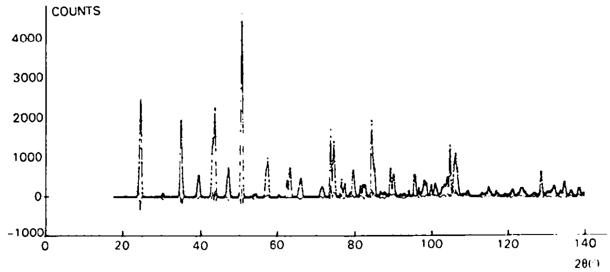

Fig. 1. The observed, (final) calculated, and difference intensity scans from 2θ = 18·05 to 140·00° in steps of 0·05°, neutron wavelength = 1·9090 (1) Å, for phase III KIO_3 at 300 K. The observed points are represented by oblique crosses, the calculated and difference profiles by continuous (fine) lines; the latter show beneath the peaks. All are plotted relative to the same origin.

Table 1. *Atomic positional parameters of* KIO_3 *phase* III *at* 300 K *as determined by neutron powder profile structure refinement with wavelength* 1·9090 (1) Å

Standard deviations are in parentheses and the positional parameters without deviations were used to define the origin. B_{eq} values are from the anisotropic temperature parameters of Kalinin *et al.* (1978) (here *not* refined).

	x	y	z	B_{eq}(Å^2)
K(1)	0·0056 (67)	0·0220 (58)	0·4934 (68)	2·2
K(2)	−0·0017 (64)	0·4971 (73)	0·0164 (77)	2·1
K(3)	0·5225 (59)	−0·0026 (72)	0·0454 (67)	2·1
K(4)	0·5199 (72)	0·5203 (70)	0·5438 (64)	1·9
I(1)	0·0000	0·0000	0·0000	1·0
I(2)	0·0074 (55)	0·5203 (49)	0·5266 (59)	0·9
I(3)	0·5166 (51)	−0·0099 (54)	0·5185 (49)	1·0
I(4)	0·5060 (61)	0·4864 (53)	0·0192 (50)	0·9
O(11)	0·0791 (59)	−0·1694 (62)	−0·1414 (69)	4·3
O(12)	0·7881 (67)	−0·2133 (55)	−0·0020 (69)	4·4
O(13)	0·8722 (82)	0·0587 (75)	−0·1828 (74)	2·9
O(21)	0·0489 (70)	0·3382 (66)	0·3173 (71)	3·7
O(22)	0·8081 (53)	0·3345 (60)	0·5287 (59)	2·9
O(23)	0·8413 (70)	0·5776 (53)	0·3481 (69)	4·2
O(31)	0·5166 (61)	−0·1829 (58)	0·3076 (57)	3·5
O(32)	0·3619 (71)	−0·2001 (51)	0·5648 (68)	3·0
O(33)	0·2942 (60)	0·0157 (59)	0·3689 (60)	3·2
O(41)	0·3637 (51)	0·3450 (50)	0·1177 (54)	3·5
O(42)	0·3098 (60)	0·4900 (57)	−0·1780 (57)	3·8
O(43)	0·5624 (68)	0·3083 (62)	−0·1305 (62)	3·3

The profile-structure-refinement method was used to analyse the powder diffraction data obtained. The least-squares refinement program of Rietveld (1969), with modification for anisotropic thermal motion (Hewat, 1973), was used. In the refinements, two sets of parameters could be refined: those describing the characteristics of the diffractometer and those describing the crystal structure. The former group consists of five parameters: the counter zero point, the three half-width parameters and an asymmetry parameter. The structural parameters include a scale factor, the lattice constants, the fractional coordinates and thermal parameters for each atom.

The starting structural model was that obtained from single-crystal X-ray studies of Kalinin *et al.* (1978) and the initial values for lattice constants, positional coordinates, and anisotropic thermal parameters were set to their refined values. Using the background-corrected neutron data, the least-squares refinement procedure followed a well behaved path, with decreasing R-factor magnitudes, as additional parameters were released. When all except the anisotropic thermal parameters were varied, the refinement converged with R_p = 11·62, $R_{\omega p}$ = 12·73, R_I = 7·5, and R_E = 3·07%, $(\Delta/\sigma)_{\max}$ = 3·96, largest structural correlation matrix element 0·73. The observed, (final) calculated, and difference scans are presented in Fig. 1.*

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* The measured intensity (point) profile as a function of scattering angle and a list of structural factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39630 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°) *for phase* III KIO_3 *at* 300 K

IO_3 groups							
I(1)–O(11)	1·82 (5)	I(2)–O(21)	1·97 (7)	I(3)–O(31)	1·74 (6)	I(4)–O(41)	1·82 (7)
O(12)	1·90 (5)	O(22)	1·74 (6)	O(32)	1·79 (7)	O(42)	1·77 (6)
O(13)	1·72 (6)	O(23)	1·83 (7)	O(33)	1·84 (6)	O(43)	1·77 (7)
···O(41)	2·76 (4)	···O(11)	2·61 (6)	···O(13)	2·68 (7)	···O(23)	2·63 (6)
···O(33)	2·93 (5)	···O(32)	2·72 (7)	···O(43)	2·82 (6)	···O(31)	2·74 (6)
···O(21)	2·75 (5)	···O(42)	2·81 (6)	···O(22)	2·82 (6)	···O(12)	2·71 (7)
O(11)O(12)	2·78 (8)	O(21)O(22)	2·86 (8)	O(31)O(32)	2·66 (8)	O(41)O(42)	2·83 (7)
O(13)	2·77 (9)	O(23)	2·82 (8)	O(33)	2·71 (8)	O(43)	2·83 (7)
O(12)O(13)	2·90 (9)	O(22)O(23)	2·68 (8)	O(32)O(33)	2·65 (7)	O(42)O(43)	2·75 (8)
O(11)–I(1)–O(12)	96·6 (2·2)	O(21)–I(2)–O(22)	101·0 (2·6)	O(31)–I(3)–O(32)	97·9 (2·8)	O(41)–I(4)–O(42)	103·9 (3·0)
O(11)–I(1)–O(13)	102·6 (2·8)	O(21)–I(2)–O(23)	96·2 (2·6)	O(31)–I(3)–O(33)	98·4 (2·6)	O(41)–I(4)–O(43)	104·7 (3·0)
O(12)–I(1)–O(13)	106·5 (2·4)	O(22)–I(2)–O(23)	97·3 (2·9)	O(32)–I(3)–O(33)	93·9 (2·8)	O(41)–I(4)–O(43)	102·2 (2·7)
K polyhedra							
K(1)–O(33)	2·72 (8)	K(2)–O(43)	2·82 (6)	K(3)–O(31)	2·81 (8)	K(4)–O(41)	2·74 (6)
O(23)	2·88 (6)	O(13)	2·86 (8)	O(11)	2·85 (6)	O(32)	2·80 (8)
O(13)	2·98 (9)	O(21)	2·94 (9)	O(12)	3·05 (8)	O(12)	2·92 (6)
O(42)	3·08 (5)	O(22)	3·16 (7)	O(43)	3·10 (8)	O(21)	3·02 (7)
O(21)	3·14 (8)	O(23)	3·16 (9)	O(32)	3·11 (7)	O(22)	3·04 (8)
O(31)	3·14 (7)	O(11)	3·16 (9)	O(22)	3·16 (6)	O(42)	3·12 (8)
O(12)	3·16 (7)	O(12)	3·18 (8)	O(42)	3·24 (6)	O(33)	3·25 (7)
O(22)	3·24 (7)	O(42)	3·24 (8)	O(41)	3·27 (7)	O(23)	3·30 (9)
O(11)	3·56 (8)	O(31)	3·33 (6)	O(21)	3·41 (6)	O(31)	3·36 (8)
		O(41)	3·36 (7)	O(33)	3·51 (8)	O(43)	3·41 (8)
		O(33)	3·38 (6)			O(13)	3·49 (7)
		O(32)	3·56 (7)			O(11)	3·57 (6)

Efforts to include the anisotropic thermal parameters at this point caused the *R*-factor magnitudes to increase and gave unreasonable (including some negative diagonal element) thermal-parameter magnitudes. It is known that such problems are likely to occur due to inadequacy of the background-allowance method (Baharie & Pawley, 1982) and therefore further refinements, including these parameters (not here a primary objective), were not attempted.

Discussion. The results of the profile-structure-refinement method are shown in Table 1, and include the atomic positional parameters and equivalent Debye–Waller temperature factors [obtained from the X-ray anisotropic thermal parameters of Kalinin *et al.* (1978), and here *not* refined]. Table 2 lists the corresponding interatomic distances and angles for the IO_3 groups and distances for the K polyhedra. Fig. 2 shows a stereoview of the unit-cell contents, viewed approximately along the [111] direction. The pseudo-rhombohedral symmetry of the atomic arrangement and existence of a unique polar direction are apparent.

The previous uncertainty of the phase III KIO_3 structure is now resolved, since the present determination clearly supports that proposed by Kalinin *et al.* (1978) from single-crystal X-ray data, with reasonably good overall agreement (considering the likely better structural resolution for 2500 independent X-ray reflections compared to the 716 independent reflections of the present neutron powder data). Further confirmation was obtained when, on attempting refinement of Hamid's (1973) structure, it was found that, although the refinement did not become unstable, the *R*-factor magnitudes remained unacceptably large ($R_p \simeq 47$, $R_{wp} \simeq 60$, $R_I \simeq 44\%$) and unreasonable I—O interatomic distances persisted. This indicates the possible presence of a refinement 'false minimum' and the consequent incorrect structure.

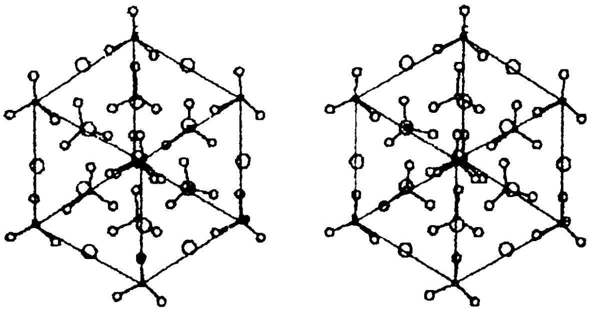

Fig. 2. A stereoview of the unit-cell contents, viewed approximately along the [111] direction and *c* axis vertical, with IO_3 groups distinguished. The atoms are represented by circles of reducing size: K, O, I, respectively.

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Hexapraseodymium Heptanickel Tetrasilicide, $Pr_6Ni_7Si_4$, an Intergrowth of $ThSi_2$- and $Y_3Rh_2Si_2$-Type Slabs

BY E. HOVESTREYDT AND E. PARTHÉ

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

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Abstract. $M_r = 1368{\cdot}76$, $oP68$, orthorhombic, $Pbcm$, $a = 5{\cdot}888$ (1), $b = 7{\cdot}4265$ (9), $c = 29{\cdot}558$ (8) Å, $V = 1292{\cdot}6$ (2) Å^3, $Z = 4$, $D_x = 7{\cdot}033$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 32{\cdot}24$ mm^{-1}, $F(000) = 2424$, room temperature, final $R = 0{\cdot}026$ for 1011 contributing reflections. The $Pr_6Ni_7Si_4$ structure can be considered as an intergrowth of $ThSi_2$- and $Y_3Rh_2Si_2$-type slabs. It is built up exclusively of trigonal prisms formed by Pr atoms and centered by Ni or Si atoms. Apart from the central part of the $ThSi_2$ slab, the structure obeys the waist-contact restriction rule. $Ce_6Ni_7Si_4$ [$a = 5{\cdot}942$ (2), $b = 7{\cdot}438$ (2), $c = 29{\cdot}24$ (1) Å], and $Nd_6Ni_7Si_4$ [$a = 5{\cdot}819$ (2), $b = 7{\cdot}414$ (3), $c = 29{\cdot}66$ (1) Å] are isotypic with $Pr_6Ni_7Si_4$.

Introduction. Systems of rare-earth element–transition element–silicon are characterized by an unusually large number of ternary compounds (Parthé & Chabot, 1984). For example, there are 21 known phases of Ce–Ni–Si (Bodak, Mis'kiv, Tyvanchuk, Kharchenko & Gladyshevskii, 1973). Recently, two additional ternary phases were discovered in this system: $Ce_2Ni_3Si_5$ (Chabot & Parthé, 1984) of $U_2Co_3Si_5$ type and $Ce_{14}Ni_6Si_{11}$ (Hovestreydt, 1984) of monoclinic $Pr_{14}Ni_6Si_{11}$ type. Mis'kiv (1973) reported on an unknown orthorhombic phase with approximate composition $Ce_{\sim10}Ni_{\sim12}Si_{\sim3}$ with space group $Pbcm$ and lattice constants $a = 5{\cdot}97$, $b = 7{\cdot}50$ and $c = 29{\cdot}2$ Å. An orthorhombic phase with this unit cell was also reported by Bodak, Mis'kiv, Tyvanchuk, Kharchenko & Gladyshevskii (1973), but with approximate composition $Ce_{\sim8}Ni_{\sim9}Si_{\sim3}$. This paper reports on the structure and composition of this compound and other phases isotypic with it.

Table 1. *Atomic positions and thermal parameters* (Å^2 × 100) *for* $Pr_6Ni_7Si_4$ *with space group Pbcm*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. E.s.d.'s are given in parentheses.

		x	y	z	U_{eq}
Si(1)	8(*e*)	0·1111 (7)	0·7299 (5)	0·1734 (1)	1·00 (9)
Pr(1)	8(*e*)	0·1126 (1)	0·38186 (9)	0·07991 (2)	1·00 (2)
Ni(1)	8(*e*)	0·1496 (3)	0·0951 (2)	0·01836 (5)	1·19 (4)
Ni(2)	8(*e*)	0·1611 (3)	0·0289 (2)	0·14775 (5)	1·17 (5)
Si(2)	8(*e*)	0·3929 (6)	0·0351 (4)	0·0823 (1)	1·01 (9)
Pr(2)	8(*e*)	0·3948 (1)	0·38797 (9)	0·18110 (2)	1·12 (2)
Ni(3)	8(*e*)	0·6474 (3)	0·2418 (2)	0·10996 (5)	1·17 (4)
Pr(3)	4(*d*)	0·1276 (2)	0·0205 (1)	0·25	1·11 (3)
Ni(4)	4(*d*)	0·6851 (5)	0·1751 (3)	0·25	1·46 (7)
Pr(4)	4(*c*)	0·6236 (2)	0·25	0	0·97 (3)

Experimental. Preparation of compounds of nominal composition $R_{10}Ni_{12}Si_3$ (R = Ce, Pr, Nd) from R (99·9%), Ni (99·99%) and Si (99·999%) by arc melting under Ar. Wrapped in Ta foil in quartz tubes at 1200 K for 1 d, at 1100 K for 26 d. From crushed sample of Pr alloy prismatic-shaped single crystal, h, l_1, l_2, l_3 = 80, 64, 80, 96 μm; automatic four-circle diffractometer (Philips PW 1100); lattice parameters from 28 reflections with $21 < \theta < 27°$; experimental absorption correction ($3{\cdot}80 < \mathrm{EAC} < 5{\cdot}98$) from 58 reflections, each at 13 different ψ settings (Flack, 1977); $\sin\theta/\lambda < 0{\cdot}64$ Å^{-1}; standard reflections 029, 506, 130 with intensity variation $< 1{\cdot}5\sigma$; 4294 reflections measured, h, k, l positive up to 7, 9, 37 with antireflections, ω–2θ scan, 1439 unique reflections ($R_{int} = 0{\cdot}024$), 1011 reflections with $I > 3\sigma(I)$, 428 unobserved; Pr-atom positions from direct methods. Ni and Si from difference Fourier synthesis, composition found to be $Pr_6Ni_7Si_4$; 82 variables refined using F values; R

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