slight decay of the crystal. Positions of six independent Pb atoms were determined by direct methods ($R = 0{\cdot}15$). $Pb(NO_2)_2.2H_2O$(?), triangular or trapezoidal plates, rapid decay of the crystals by X-ray irradiation, orthorhombic(?), $a = 11{\cdot}884$ (3), $b = 38{\cdot}988$ (37), $c = 9{\cdot}201$ (2) Å, $V = 4263$ (4) Å^3, $Z = 28$ (?).

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Structure (Neutron) of Potassium Iodate at 100 and 10 K

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Abstract. KIO_3, $M_r = 214{\cdot}001$, $P1$, $Z = 4$, neutron powder diffraction (Rietveld method), $\lambda = 1{\cdot}9090$ (1) Å, $F(000) = 320$, $D_m(300\ \mathrm{K}) = 3{\cdot}89\ \mathrm{g\ cm^{-3}}$; at $T = 100$ K: $a = 7{\cdot}6982$ (4), $b = 7{\cdot}6597$ (2), $c = 7{\cdot}6912$ (5) Å, $\alpha = 108{\cdot}999$ (5), $\beta = 109{\cdot}745$ (2), $\gamma = 109{\cdot}085$ (5)°, $V = 351{\cdot}60$ (2) Å^3, $D_x = 4{\cdot}04\ \mathrm{g\ cm^{-3}}$, $R_I = 8{\cdot}12\%$ for 799 integrated Bragg intensities; at $T = 10$ K: $a = 7{\cdot}6818$ (5), $b = 7{\cdot}6504$ (3), $c = 7{\cdot}6896$ (5) Å, $\alpha = 109{\cdot}062$ (5), $\beta = 109{\cdot}786$ (2), $\gamma = 109{\cdot}012$ (5)°, $V = 350{\cdot}22$ (3) Å^3, $D_x = 4{\cdot}06\ \mathrm{g\ cm^{-3}}$, $R_I = 7{\cdot}95\%$ for 786 integrated Bragg intensities. The previously reported phase transitions to phase IV (below 263 K) and phase V (below 83 K) [Herlach (1961). *Helv. Phys. Acta*, **34**, 305–330] are found not to involve significant atomic-scale change to the room-temperature phase III triclinic structure. The observed marked variations in the ferroelectric behaviour that prompted the transitions proposal are considered to originate from domain- or twin-scale changes within the sample.

Introduction. At atmospheric pressure, potassium iodate has been reported (from nuclear quadrupole resonance, dielectric constant, and X-ray powder diffraction measurements) to undergo phase transitions with temperature change:

$$\mathrm{V} \xleftrightarrow{83\mathrm{K}} \mathrm{IV} \underset{263\mathrm{K}}{\overset{255\mathrm{K}}{\rightleftarrows}} \mathrm{III} \xleftrightarrow{343\mathrm{K}} \mathrm{II} \xleftrightarrow{485\mathrm{K}} \mathrm{I}$$

and all phases, except I, are ferroelectric (Herlach, 1961).

Recently the room-temperature phase III has been shown by neutron diffraction to have a triclinic structure, with very pronounced pseudorhombohedral symmetry (Lucas, 1984). No structural information on the reported lower-temperature phases (IV and V) has been published to date and therefore the present study was made to investigate this, using the neutron powder profile method.

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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 temperatures 100 and 10 K; high-resolution neutron powder diffractometer (*D*1*A*) at the high-flux reactor of the Institut Laue–Langevin (ILL) (Grenoble); *D*1*A* has a bank of ten ^{3}He high-pressure counters with a 6° angular separation. Resultant intensity profile at each temperature (100 and 10 K) obtained by appropriately combining the intensities from these counters to cover an effective 2θ range of 6·00 to 160·00° in 0·05° steps. Backgrounds under the diffraction peaks estimated by linear interpolation between points chosen in those regions devoid of reflections and subtracted from the total observed profiles. No regions omitted within the 2θ scans. Scattering lengths: $b_{\rm K} = 3\cdot7$, $b_{\rm I} = 5\cdot3$ and $b_{\rm O} = 5\cdot83$ fm (Bacon, 1975; Schneider, 1976).

The profile-structure-refinement method was used to analyse the powder diffraction data sets obtained at each temperature. 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 2θ 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 similarity of the profile patterns obtained at 100 and 10 K to each other and to the room-temperature (phase III) profile, together with the fact that the latter structure was shown recently to be triclinic (Lucas, 1984), suggested that the structural phase changes below room temperature are small or even non-existent.

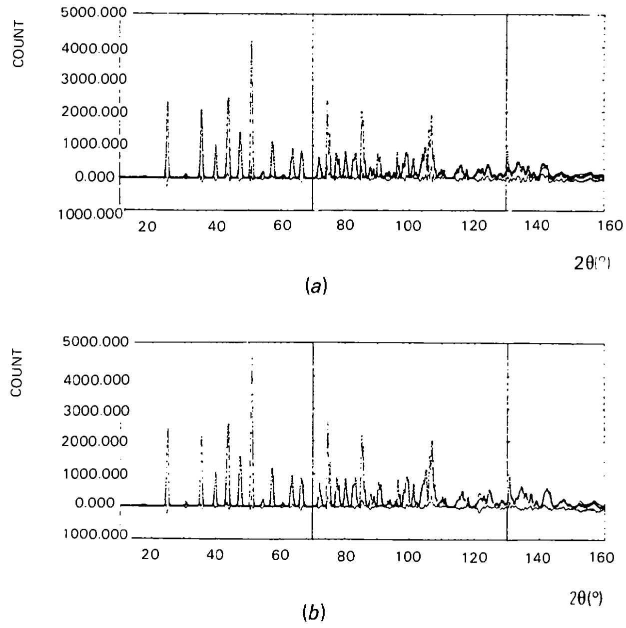

Fig. 1. The observed, (final) calculated, and difference intensity scans from $2\theta = 6\cdot00$ to 160·00° in steps of 0·05°, neutron wavelength = 1·9090 (1) Å, for KIO_3 at (*a*) 100 K and (*b*) 10 K. The observed points are represented by oblique crosses, the calculated and difference profiles by continuous (fine) lines; the latter shows beneath the peaks. All are plotted relative to the same origin.

Table 1. *Atomic positional parameters of* KIO_3 *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 define the origin. The first row of numbers for each atom are 100 K values, immediately beneath are those for 10 K. Like element-type atomic isotropic temperature parameters were constrained to be equal during refinements.

	x	*y*	*z*	*B*(Å^2)
K(1)	−0·0063 (51) −0·0520 (49)	0·0266 (45) 0·0389 (39)	0·4832 (59) 0·5042 (47)	
K(2)	−0·0135 (68) −0·0001 (58)	0·4926 (61) 0·4989 (54)	0·0022 (70) −0·0119 (55)	
				0·52 (13) 0·34 (10)
K(3)	0·5117 (48) 0·5012 (44)	−0·0027 (34) 0·0172 (42)	0·0277 (53) 0·0166 (47)	
K(4)	0·5014 (56) 0·5023 (54)	0·5131 (62) 0·5281 (54)	0·5435 (66) 0·5212 (62)	
I(1)	0·0000 0·0000	0·0000 0·0000	0·0000 0·0000	
I(2)	−0·0128 (44) −0·0112 (41)	0·5109 (35) 0·5229 (35)	0·5060 (46) 0·4890 (41)	
				0·33 (6) 0·07 (8)
I(3)	0·4898 (49) 0·4775 (47)	0·0002 (50) 0·0200 (55)	0·5208 (50) 0·5092 (46)	
I(4)	0·5032 (45) 0·4891 (37)	0·4879 (36) 0·5009 (38)	0·0096 (42) 0·0035 (38)	
O(11)	0·0697 (52) 0·0650 (44)	−0·1727 (41) −0·1699 (41)	−0·1360 (46) −0·1229 (41)	
O(12)	0·7789 (44) 0·7668 (41)	−0·1952 (39) −0·1819 (46)	0·0040 (45) −0·0169 (40)	
O(13)	0·8567 (46) 0·8380 (37)	0·0379 (47) 0·0304 (42)	−0·2163 (50) −0·2217 (36)	
O(21)	0·0308 (40) 0·0216 (35)	0·3478 (36) 0·3622 (37)	0·3028 (45) 0·2938 (36)	
O(22)	0·7896 (46) 0·7687 (41)	0·3167 (38) 0·3270 (37)	0·5014 (42) 0·4976 (39)	
O(23)	0·8542 (41) 0·8298 (39)	0·6065 (35) 0·6192 (39)	0·3518 (43) 0·3591 (40)	
				0·94 (3) 0·45 (3)
O(31)	0·4987 (45) 0·4910 (34)	−0·1746 (39) −0·1666 (35)	0·2867 (45) 0·2914 (35)	
O(32)	0·3648 (48) 0·3249 (48)	−0·1920 (45) −0·1852 (43)	0·5799 (51) 0·5628 (42)	
O(33)	0·2909 (46) 0·2745 (44)	0·0333 (38) 0·0601 (45)	0·3685 (41) 0·3687 (47)	
O(41)	0·3535 (55) 0·3549 (42)	0·3207 (48) 0·3229 (44)	0·0935 (50) 0·0820 (39)	
O(42)	0·2839 (38) 0·2747 (39)	0·4591 (31) 0·4706 (35)	−0·2000 (40) −0·2091 (39)	
O(43)	0·5678 (44) 0·5778 (43)	0·3078 (40) 0·3420 (42)	−0·1335 (45) −0·1366 (42)	

The starting structural model for each temperature data set was therefore the phase III structure, and the initial values for lattice constants, positional coordinates, and isotropic thermal parameters were set to the refined values (Lucas, 1984). Using the background-corrected neutron data for each temperature, the least-squares refinement procedures followed well behaved paths, with decreasing R-factor magnitudes, as additional parameters were released. The refinements converged with the following details:

(i) $T = 100$ K: $R_p = 10{\cdot}58$, $R_{wp} = 10{\cdot}70$, $R_I = 8{\cdot}12$ and $R_E = 2{\cdot}34\%$, $(\Delta/\sigma)_{\max} = 4{\cdot}63$, largest structural correlation-matrix element $[\mathrm{CM}]_{ij} = 0{\cdot}82$.

(ii) $T = 10$ K: $R_p = 10{\cdot}31$, $R_{wp} = 10{\cdot}80$, $R_I = 7{\cdot}95$ and $R_E = 2{\cdot}17\%$, $(\Delta/\sigma)_{\max} = 5{\cdot}83$, $[\mathrm{CM}]_{ij} = 0{\cdot}72$.

The observed, (final) calculated, and difference scans for (*a*) 100 K and (*b*) 10 K are shown in Fig. 1.*

The refinements included isotropic thermal parameters constrained to equal values for each element-type atom, as attempts to refine individual isotropic temperature factors resulted in some physically unrealistic (negative) magnitudes.

Discussion. The final parameter values obtained by the profile-structure-refinement method are shown in Table 1. 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 results show that the reported transitions to phase IV (below 263 K) and phase V (below 83 K) do not involve significant atomic-scale change to the room-temperature phase III triclinic structure (Lucas, 1984), which persists down to at least 10 K.

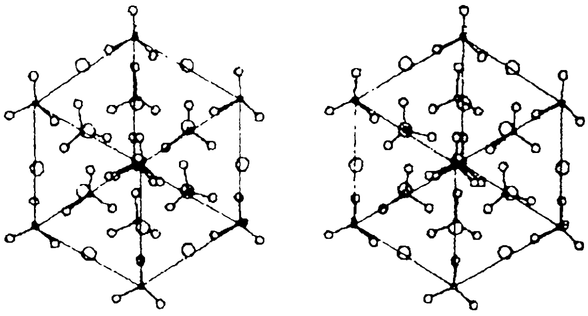

Fig. 2. A stereoview of the unit-cell contents, viewed approximately along the [111] direction and *c* axis vertical, with IO_3 groups distinguished. The atoms are represented by circles of reducing size: K, O, I, respectively.

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* KIO_3 *at* 100 K (*first column*) *and* 10 K (*second column*)

IO_3 groups

I(1)–O(11)	1·75 (4)	1·66 (4)	I(2)–O(21)	1·86 (5)	1·76 (4)	I(3)–O(31)	1·90 (5)	1·87 (5)	I(4)–O(41)	1·86 (6)	1·82 (5)
O(12)	1·88 (3)	1·81 (3)	O(22)	1·73 (5)	1·90 (4)	O(32)	1·76 (6)	1·89 (5)	O(42)	1·78 (4)	1·77 (4)
O(13)	1·83 (4)	1·88 (3)	O(23)	1·80 (5)	1·81 (5)	O(33)	1·74 (5)	1·76 (5)	O(43)	1·79 (5)	1·81 (5)
···O(41)	2·67 (4)	2·71 (3)	···O(11)	2·71 (5)	2·85 (4)	···O(13)	2·72 (5)	2·80 (5)	···O(23)	2·66 (4)	2·67 (4)
···O(33)	2·82 (3)	2·68 (4)	···O(32)	2·77 (5)	2·53 (5)	···O(43)	2·63 (5)	2·65 (5)	···O(31)	2·78 (5)	2·77 (4)
···O(21)	2·78 (3)	2·86 (3)	···O(42)	2·86 (4)	2·85 (4)	···O(22)	2·83 (5)	2·72 (5)	···O(12)	2·68 (5)	2·75 (5)
O(11)–O(12)	2·77 (6)	2·66 (5)	O(21)–O(22)	2·78 (5)	2·88 (5)	O(31)–O(32)	2·80 (6)	2·81 (5)	O(41)–O(42)	2·76 (5)	2·80 (5)
O(13)	2·71 (6)	2·75 (5)	O(23)	2·75 (5)	2·83 (5)	O(33)	2·68 (5)	2·83 (5)	O(43)	2·78 (6)	2·78 (5)
O(12)–O(13)	2·89 (6)	2·66 (5)	O(22)–O(23)	2·80 (5)	2·75 (5)	O(32)–O(33)	2·79 (5)	2·79 (6)	O(42)–O(43)	2·77 (5)	2·77 (5)

O(11)–I(1)–O(12)	99·5 (1·6)	100·2 (1·6)	O(31)–I(3)–O(32)	99·7 (2·3)	96·6 (2·2)
O(11)–I(1)–O(13)	98·4 (1·7)	101·8 (1·5)	O(31)–I(3)–O(33)	94·8 (2·2)	102·4 (2·1)
O(12)–I(1)–O(13)	102·5 (1·6)	92·6 (1·5)	O(32)–I(3)–O(33)	105·8 (2·5)	100·2 (2·4)
O(21)–I(2)–O(22)	101·2 (1·9)	104·1 (1·7)	O(41)–I(4)–O(42)	98·5 (2·1)	102·5 (1·9)
O(21)–I(2)–O(23)	97·2 (2·3)	105·3 (2·1)	O(41)–I(4)–O(43)	99·3 (2·2)	99·7 (2·2)
O(22)–I(2)–O(23)	105·2 (2·2)	95·8 (2·0)	O(42)–I(4)–O(43)	101·7 (2·0)	101·4 (1·9)

K polyhedra

K(1)–O(33)	2·71 (6)	3·00 (6)	K(2)–O(43)	2·70 (6)	2·74 (5)	K(3)–O(31)	2·73 (6)	2·90 (5)	K(4)–O(41)	2·89 (6)	2·82 (5)
O(23)	2·72 (4)	2·73 (4)	O(13)	2·95 (6)	2·99 (5)	O(11)	2·83 (5)	2·80 (5)	O(32)	2·76 (7)	2·92 (6)
O(13)	2·84 (7)	2·53 (5)	O(21)	2·84 (7)	2·85 (6)	O(12)	2·92 (5)	2·95 (5)	O(12)	2·95 (6)	2·95 (5)
O(42)	2·85 (5)	2·86 (5)	O(22)	3·21 (6)	3·13 (5)	O(43)	3·00 (5)	3·06 (5)	O(21)	3·02 (5)	3·07 (5)
O(21)	3·18 (6)	3·37 (5)	O(23)	3·15 (7)	3·51 (6)	O(32)	2·88 (5)	2·88 (5)	O(22)	3·11 (6)	2·95 (6)
O(31)	3·15 (5)	2·88 (5)	O(11)	3·05 (7)	2·88 (6)	O(22)	3·06 (5)	3·08 (5)	O(42)	3·03 (7)	3·18 (6)
O(12)	3·03 (5)	3·33 (5)	O(12)	3·28 (7)	3·47 (6)	O(42)	3·41 (4)	3·46 (4)	O(33)	3·06 (5)	3·01 (5)
O(22)	3·11 (6)	2·96 (5)	O(42)	3·20 (7)	3·01 (6)	O(41)	3·07 (6)	2·88 (5)	O(23)	3·49 (6)	3·15 (6)
O(11)	3·69 (6)	3·71 (5)	O(31)	3·29 (6)	3·17 (5)	O(21)	3·35 (5)	3·34 (5)	O(31)	3·56 (7)	3·36 (6)
O(32)	3·74 (6)	3·79 (6)	O(41)	3·45 (7)	3·39 (6)	O(33)	3·56 (6)	3·67 (6)	O(43)	3·33 (7)	
O(41)		3·75 (5)	O(33)	3·49 (6)	3·63 (6)	O(13)	3·73 (6)	3·64 (5)	O(13)	3·41 (6)	3·23 (5)
			O(32)	3·70 (6)	3·64 (6)				O(11)	3·60 (6)	3·59 (6)

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* The measured intensity (point) profile as a function of scattering angle and a list of integrated squared structure factors for both 100 and 10 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42293 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Herlach (1961) proposed the phase transitions to IV and V from the observed changes in the ferroelectric behaviour as the temperature was reduced. Marked variations of the observed resonance-line intensities in the nuclear quadrupole resonance and dielectric constant (hysteresis loop size and shape in the Sawyer & Tower method) measurements, with temperature decrease, were cited as evidence of the transitions, although no significant changes to the X-ray powder diffraction pattern were observed.

The sample used was presumed to be a single crystal, although it is well known (Náray-Szabó & Kálmán, 1961) that twinned crystals are almost invariably produced in growth. A twinned crystal, or one with large ferroelectric domains (the electric Barkhausen effect was observed), under time-varying external magnetic or electric fields could produce the observed (nuclear quadrupole resonance and dielectric constant) variations, with the observed phenomena arising from temperature-induced changes at this scale, rather than at the atomic level.

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Structure of the New Zeolite Theta-1 Determined from X-ray Powder Data

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Abstract. SiO_2, $M_r = 60{\cdot}1$, orthorhombic, $Cmc2_1$, $a = 13{\cdot}836\ (3)$, $b = 17{\cdot}415\ (4)$, $c = 5{\cdot}042\ (1)$ Å, $U = 1215$ Å^3, $Z = 24$, $D_x = 1{\cdot}97\ \mathrm{g\ cm^{-3}}$, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 72\ \mathrm{cm^{-1}}$, $F(000) = 720$, $T = 293$ K, $R = 0{\cdot}116$ for 213 reflections with $I > 2\sigma(I)$. The structure was determined by structure modelling based upon two-dimensional Fourier projections; the intensities of the multiple overlapping reflections were extracted from the powder pattern. Conventional 'single-crystal-type' refinement techniques were used. The Si—Si bond distances and the geometry of the SiO_4 tetrahedra were as expected. Theta-1 is the first reported unidimensional medium-pore high-silica zeolite and it represents a new, topologically distinct, structure type.

Introduction. Synthetic high-silica zeolites exhibit a combination of properties which make them unique both scientifically and commercially. Physicochemical and catalytic studies of the new zeolite theta-1 indicated (Barri, Smith, White & Young, 1984) properties typical of a high-silica zeolite: it was thermally stable, shape-selective and had acidic properties. Their results also showed a bulk SiO_2:Al_2O_3 molar ratio of 60:1, and that the zeolite was microporous with slightly elliptical pores of approximately 6 Å diameter. The present crystallographic study was undertaken to determine the structure unequivocally. It is notoriously difficult to synthesize large (*i.e.* >100 μm) single crystals of high-silica zeolites. Theta-1 is no exception. The typical size of the largest capped needle prisms was $0{\cdot}1 \times 2$ μm. Therefore, since conventional X-ray structural methods were not appropriate, X-ray powder data were collected and used to derive, and refine, a trial structure.

Experimental. Theta-1 crystals were grown from a gel system as described elsewhere (European patent No. 0057049; published European patent application No. 0104800). Data were collected using a 17 cm vertical diffractometer, graphite monochromator, proportional counter, divergence slits ($\frac{1}{4}$° used for 5–14° 2θ, $\frac{1}{2}$° for 11–29°, 1° for 22–51° and 2° for 42–140°), Soller slits, $\frac{1}{2}$° receiving slit, instrumental profile breadth $0{\cdot}15$° (2θ), back-loaded sample, step scan, $0{\cdot}02$° steps,

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