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Structure (Neutron) of High-Temperature Phase I Potassium Iodate at 523 K

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Abstract. KIO_3, $M_r = 214{\cdot}001$, $R3$ (refinement preferred with O atoms at x, y, z; rather than x, x, z required for $R3m$), $a = 4{\cdot}4973\,(1)$ Å, $\alpha = 89{\cdot}218\,(2)°$, $V = 90{\cdot}94\,(1)$ Å^3, $Z = 1$, $D_m(300\,\text{K}) = 3{\cdot}89$, $D_x = 3{\cdot}91$ g cm^{-3}, neutron powder diffraction (Rietveld method), $\lambda = 1{\cdot}384\,(1)$ Å, $F(000) = 80$, $T = 523$ K, $R_I = 7{\cdot}79\%$ for 183 integrated Bragg intensities. The room-temperature triclinic (pseudo-rhombohedral) phase III structure transforms to the rhombohedral (pseudo-cubic) phase I structure by displacements of K and I atoms by approximately 0·1 Å, O atoms by approximately 0·2 Å, and the slightly distorted IO_3 groups in phase III become regular about threefold symmetry axes in phase I.

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

$$\mathrm{V} \xrightarrow{83\,\mathrm{K}} \mathrm{IV} \underset{263\,\mathrm{K}}{\overset{255\,\mathrm{K}}{\leftrightarrows}} \mathrm{III} \xrightarrow{343\,\mathrm{K}} \mathrm{II} \xrightarrow{485\,\mathrm{K}} \mathrm{I}$$

and all phases, except I, have been reported to be ferroelectric (Herlach, 1961). Recently, the crystal structures from room temperature down to 10 K have been determined by high-resolution neutron powder diffraction (Lucas, 1984, 1985). Hamid (1973) proposed an $R\bar{3}m$ structure for phase I, based on X-ray powder diffraction data. This was subsequently criticized by Crane (1972, 1975), who found evidence of pyroelectricity in the phase and instead suggested an $R3m$ structure.

The aim of the present investigation was to use the neutron powder profile method to determine the structure of phase I.

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 pressures and 523 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 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. 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 from the 2θ scan. Scattering lengths: $b_K = 3{\cdot}7$, $b_I = 5{\cdot}3$ and $b_O = 5{\cdot}83$ fm (Bacon, 1975; Schneider, 1976).

The profile-structure-refinement method was used to analyse the powder diffraction data obtained. The least-squares refinement method of Rietveld (1969), with modification for anisotropic thermal motion (Hewat, 1973), was used. 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.

Preliminary refinements indicated a structure with some similarities to that proposed by Crane (1972), but with a smaller (one-eighth) unit cell, *i.e.* a rhombohedral (pseudo-cubic) unit cell with $a \simeq 4{\cdot}45$ Å and $Z = 1$. Four structural models (with space groups $R\bar{3}m$, $R\bar{3}$, $R3m$, $R3$) were each refined to the observed data. The atom positions in all models were of the type

K atom x,x,x; I atom x,x,x; O atom x,y,z;

where $x(\mathrm{I}) = 0$ (for $R\bar{3}m$ and $R\bar{3}$, chosen space-group positions; for $R3m$ and $R3$, chosen to fix the unit-cell origin), and $y(\mathrm{O}) = x(\mathrm{O})$ (for $R\bar{3}m$ and $R3m$, chosen space-group positions). The models with space groups $R\bar{3}m$ and $R\bar{3}$ also require disorder of the K and O atoms about the centre of symmetry located at the (chosen) I-atom positions, and half-atom weighting was applied for the disordered atoms. All refinements followed well behaved paths with decreasing R-factor magnitudes to convergence, but the $R\bar{3}m$ and $R\bar{3}$ models had residual factors considerably larger than those based on $R3m$ and $R3$, *viz*: for $R\bar{3}m$, $R\bar{3}$, $R3m$ and $R3$ (in space-group-model order) $R_p = 30{\cdot}84$, 29·87, 15·91, 15·87; $R_{wp} = 32{\cdot}08$, 31·17, 14·11, 13·96; $R_I = 23{\cdot}71$, 23·05, 7·82, 7·79; $R_E = 6{\cdot}43$, 6·41, 6·36, 6·36%. The $R\bar{3}m$ and $R\bar{3}$ models were thus

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rejected, while distinction between the $R3m$ and $R3$ models depends only on whether (for $R3m$) or not (for $R3$) $y(O) = x(O)$. The refined values obtained for the $R3$ model are $x(O) = 0{\cdot}0280\,(15)$ and $y(O) = 0{\cdot}0550\,(15)$, compared with $x(O) = y(O) = 0{\cdot}0408\,(5)$ for the $R3m$ model, and these differences are considered of sufficient significance to suggest preference for the $R3$ model over the $R3m$ model. The largest structural correlation-matrix element (for the $R3$ model refinement) was 0·74, $(\Delta/\sigma)_{\max} = 0{\cdot}04$. The observed, (final) calculated and difference scans are presented in Fig. 1.*

Discussion. The results of the profile structure refinement are shown in Table 1, and include the atom positions and equivalent temperature factors. 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.

Crane (1972) investigated, and summarized previous investigations of, the KIO_3 phase-transition behaviour over the temperature range 298 to 523 K. The results support a single structural phase transition at 485 K, since the only significant change in the X-ray powder pattern occurred at this temperature. Although other physical techniques, such as a nuclear quadrupole resonance (Herlach, 1961), did show some discontinuities in behaviour at other temperatures within the range, it is now considered that these observations are likely to be due to ferroelectric-domain changes with temperature change rather than structural changes at the atomic level (Lucas, 1984, 1985). Together with the very close similarity of the III and I structures, this suggests that the III→I transition is probably the only structural transition that actually occurs over the temperature range 10 K to 523 K.

The unit cell of phase III (pseudo-rhombohedral) is related to that presently proposed for phase I (pseudocubic) as follows:

$$\begin{aligned}\mathbf{a}_{\rm III} &\simeq \mathbf{a}_{\rm I} - \mathbf{b}_{\rm I} + \mathbf{c}_{\rm I}\\ \mathbf{b}_{\rm III} &\simeq \mathbf{a}_{\rm I} + \mathbf{b}_{\rm I} - \mathbf{c}_{\rm I}\\ \mathbf{c}_{\rm III} &\simeq -\mathbf{a}_{\rm I} + \mathbf{b}_{\rm I} + \mathbf{c}_{\rm I}.\end{aligned}$$

The inverse transformation is

$$\begin{aligned}\mathbf{a}_{\rm I} &\simeq 0{\cdot}5(\mathbf{a}_{\rm III} + \mathbf{b}_{\rm III})\\ \mathbf{b}_{\rm I} &\simeq 0{\cdot}5(\mathbf{b}_{\rm III} + \mathbf{c}_{\rm III})\\ \mathbf{c}_{\rm I} &\simeq 0{\cdot}5(\mathbf{c}_{\rm III} + \mathbf{a}_{\rm III}).\end{aligned}$$

Fig. 3 illustrates the relationship between the crystallographic axes of phase I and phase III, which is in general agreement with that proposed by Crane (1972).

Table 1. *Atomic positions and equivalent isotropic thermal parameters* (Å^2) *for* KIO_3 *phase* I *at* 523 K *as determined by neutron powder profile structure refinement with wavelength* 1·384 (1) Å

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j(\beta_{ij}\mathbf{a}_i.\mathbf{a}_j).$$

E.s.d.'s are in parentheses and the positional parameters without deviations were used to define the origin.

	x	y	z	B_{eq}
K	0·51117 (90)	x	x	3·85 (6)
I	0·00000	x	x	1·79 (4)
O	0·02804 (150)	0·05498 (153)	−0·39094 (47)	5·93 (24)

Table 2. *Interatomic distances* (Å) *and angles* (°) *for phase* I KIO_3 *at* 523 K

IO_3 group		K polyhedra	
I—O	1·775 (5)	K···O	3·032 (7)
O—I—O	100·8 (3)		3·111 (8)
			3·280 (7)
			3·434 (8)

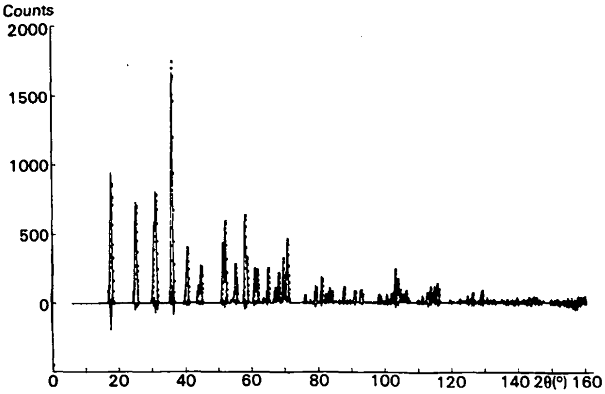

Fig. 1. The observed, (final) calculated and difference intensity scans from $2\theta = 6{\cdot}00$ to 160·00° in steps of 0·05°, neutron wavelength = 1·384 (1) Å, for phase I KIO_3 at 493 K. The observed points are represented by oblique crosses, the calculated and difference profiles by continuous (fine) lines; the latter shown beneath the peaks. All are plotted relative to the same origin.

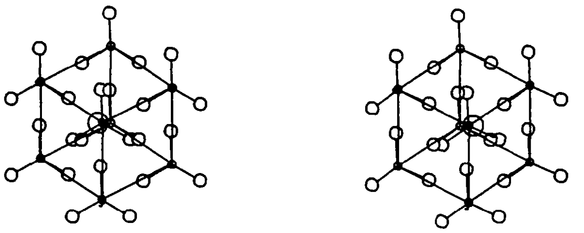

Fig. 2. A stereoview of the unit-cell contents, viewed approximately along the [111] direction with c axis vertical, with IO_3 groups distinguished. The atoms are represented by circles of reducing size: K, O, I, respectively.

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* The measured intensity (point) profile as a function of scattering angle, a list of integrated squared structure factors, the anisotropic temperature factors, and more detailed comparison of atomic position changes with phase transformation have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43977 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

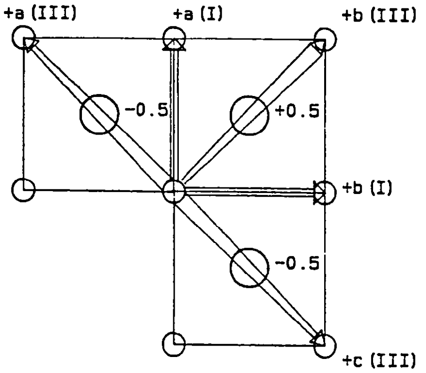

Fig. 3. A view of the unit-cell contents, with the c_I axis into the page, illustrating the transformation between the phase I structure and the phase III structure. The O atoms (I—O bonds orientated approximately along the negative direction of the phase I axes) are not shown. The I atoms are in the plane of the paper, while the atomic coordinates of the K atoms along the c_I axis are as shown. The atoms are represented by circles of decreasing size: K, I.

The triclinic symmetry of the phase III structure does not constrain the conformation of the IO_3 groups as all atoms are in general positions and some distortions of the individual groups are apparent, although the I—O bond lengths and O—I—O angles *averaged over all groups* are 1·81 (7) Å, 100·2 (3·6)° at 10 K; 1·81 (6) Å, 100·3 (3·2)° at 100 K; 1·81 (7) Å, 100·1 (3·9)° at 300 K. On transition to the rhombohedral-symmetry structure of phase I, the atoms are displaced from their phase III positions by approximately 0·1 Å for K and I atoms, approximately 0·2 Å for O atoms.* The IO_3 groups are now positioned about threefold symmetry axes, which constrain them to have the regular undistorted conformations indicated in Table 2.

The possible existence of ferroelectric-type behaviour in phase I of KIO_3 has been the subject of several investigations. Herlach (1961) reported phase I to be paraelectric, on the basis of nuclear quadrupole resonance measurements; Crane (1972) found the existence of pyroelectricity in this phase. As the present study suggests a structure with non-centrosymmetric space group $R3$, the latter observation is supported and calculation based on the proposed structure indicates an approximate spontaneous polarization of 0·16 C m^{-2}. This is comparable in magnitude to the 0·12 C m^{-2} calculated for γ-KNO_3 by Nimmo & Lucas (1976).

The previous uncertainties of the phase I KIO_3 structure, the phase-transition behaviour, and some aspects of its ferroelectric/pyroelectric properties have now been resolved.

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* See deposition footnote.

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Structure of Dithionitryl Hexafluoroarsenate(V)

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Abstract. $NS_2^+.AsF_6^-$, $M_r = 267{\cdot}04$, monoclinic, $C2/m$, $a = 9{\cdot}5542\,(13)$, $b = 6{\cdot}5968\,(14)$, $c = 5{\cdot}3017\,(11)$ Å, $\beta = 91{\cdot}15\,(2)°$, $V = 334{\cdot}1\,(2)$ Å^3, $D_x = 2{\cdot}66$ Mg m^{-3} for $Z = 2$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu(\text{Mo } K\alpha) = 5{\cdot}72$ mm^{-1}, $F(000) = 252$, $T = 293$ K. The structure was refined by full-matrix least squares to $R = 0{\cdot}041$,

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