occupancy factors for the Ce and Mo sites confirmed that they are fully occupied. All calculations were performed with the *MolEN* (Fair, 1990) programs on a Digital MicroVAX 3100.

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Structure Refinement of $Y_2Ru_2O_7$ by Neutron Powder Diffraction

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Abstract

The structure of the pyrochlore yttrium ruthenium oxide, $Y_2Ru_2O_7$, was determined by Rietveld analysis of time-of-flight neutron powder diffraction data. Each Ru atom has a nearly regular octahedral coordination environment whereas each Y atom has a distorted eightfold-coordination geometry. The JCPDS file number for yttrium ruthenium oxide is 28-1456.

Comment

A number of oxide pyrochlores, especially those incorporating Ru or Ir, exhibit high electrocatalytic activity for several oxygen-transfer reactions, including O_2 reduction or evolution (Egdell, Goodenough, Hamnett & Naish, 1983) and the oxidation of organic molecules (Felthouse, Fraundorf, Friedman & Schosser, 1991). Their activity is believed to be related to their oxygen non-stoichiometry, their general formula being given by $A_2B_2O_{7-y}$. These materials are also of interest because of the sensitivity of their electronic structure to the A-type cation. This sensitivity is believed to be a consequence of changes in both the RuO_6 geometry and the Ru t_{2g} band width.

As part of a detailed study of structural (Facer, Howard & Kennedy, 1993; Facer, Elcombe & Kennedy, 1993) and electrocatalytic (Gokagac & Kennedy, 1993, 1994) properties of metal pyrochlores, it was decided to investigate the structure of $Y_2Ru_2O_7$ in order to obtain an accurate description of the YO_8 and RuO_6 polyhedra, and to determine the anisotropy of the displacement parameters. The previously reported powder X-ray measurements were expected to be relatively insensitive to O-atom displacements and thermal vibrations (Kanno, Takeda, Yamamoto, Kawamoto & Yamamoto, 1993). The results of the structure determination of $Y_2Ru_2O_7$ using powder neutron diffraction data are reported here.

The neutron diffraction refinement of the structure of $Y_2Ru_2O_7$ confirms that the material adopts a regular pyrochlore structure (Subramanian, Aravamudan & Subba Rao, 1983). No 420 reflection was observed in the neutron and X-ray diffraction data, indicating that there was no vacancy ordering on the O2 site (Beyerlein *et al.*, 1984). Refinement proceeded in space group $Fd\bar{3}m$. Refinement of the occupancies of the Y, Ru and O sites indicated no significant deviation from the expected stoichiometry.

The refined positional parameter for the O1 atom, 0.33536 (3), is in excellent agreement with that determined by X-ray powder methods (Kanno, Takeda, Yamamoto, Kawamoto & Yamamoto, 1993). The YO_8 scalenohedron is axially compressed with six O atoms at 2.4503 (2) Å from Y and two at 2.19601 (3) Å. These Y—O bond lengths are similar to those found in $Y_2Sn_2O_7$ (Facer, Howard & Kennedy, 1993). The Ru—O distance, 1.9911 (1) Å, is slightly longer than that found in $Bi_2Ru_2O_{6.9}$ (1.974 Å; Facer, Elcombe & Kennedy, 1993), while the O—Ru—O angle has decreased to 128.45 (2)° in $Y_2Ru_2O_7$ relative to that of 133° in $Bi_2Ru_2O_{6.9}$, indicating weaker Ru—O—Ru interactions in $Y_2Ru_2O_7$. This is consistent with the semiconducting properties of $Y_2Ru_2O_7$ and metallic properties of $Bi_2Ru_2O_{6.9}$. The displacement parameters for both the Y and O1 atoms are large and highly anisotropic. For the Y atom, movement along the three-fold axis, that is towards the two closest O atoms, is

inhibited; the principal vibration is parallel to the [111] direction and is given by $U_{11} + 2U_{12} = 2.17 \times 10^{-3}$ Å^2, and is noticeably smaller than movements perpendicular to this direction ($U_{11} - U_{12} = 5.48 \times 10^{-3}$ Å^2). The displacement of O1 in the (011) plane ($U_{22} - U_{23} = 2.92 \times 10^{-3}$ Å^2) is much smaller than that in the [100] ($U_{11} = 5.35 \times 10^{-3}$ Å^2) or [011] directions ($U_{22} + U_{23} = 6.20 \times 10^{-3}$ Å^2).
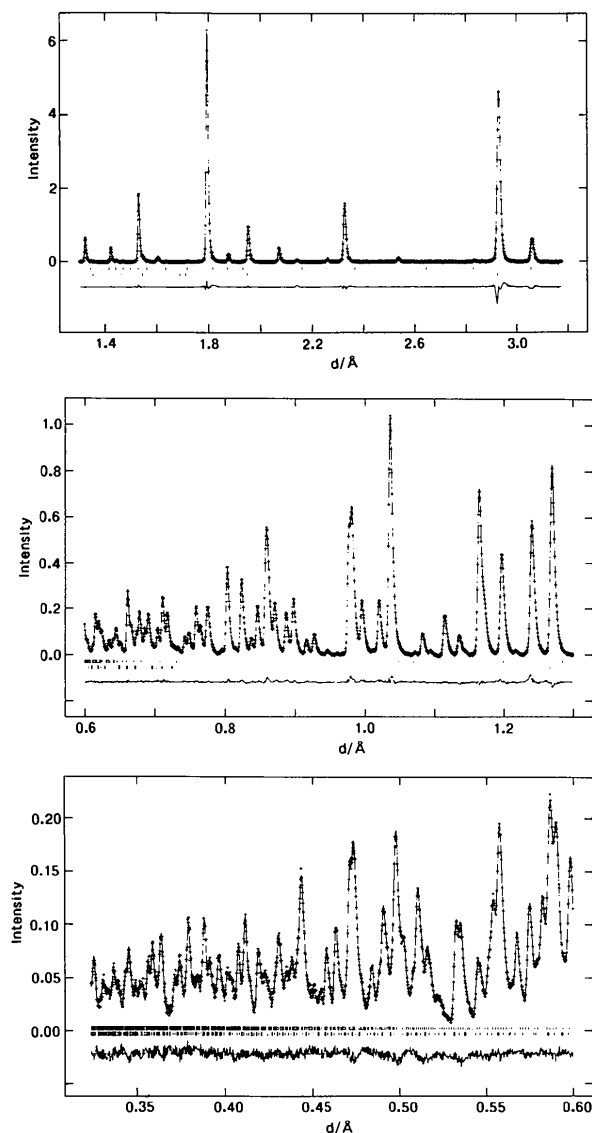

Fig. 1. Observed, calculated and difference neutron powder diffraction profiles for Y$_2$Ru$_2$O$_7$. The short vertical lines below the profiles mark the position of all possible Bragg reflections for Y$_2$Ru$_2$O$_7$ (lower) and Y$_2$O$_3$ (upper).

Experimental

A polycrystalline sample of Y$_2$Ru$_2$O$_7$ was prepared by the solid-state reaction of Y$_2$O$_3$ (Fluka) and Ru (Aldrich) at 873 K for 12 h, 1073 K for 24 h and 1473 K for 48 h with regrinding between successive firings. Only peaks due to the desired pyrochlore phase were observed in the X-ray powder diffraction pattern.

Crystal data

Y$_2$Ru$_2$O$_7$	Neutron time-of-flight
M_r = 491.95	radiation
Cubic	Cell parameters from 868
$Fd\bar{3}m$	reflections
a = 10.1429 (2) Å	T = 295 K
V = 1043.48 Å^3	Black
Z = 8	
D_x = 6.26 Mg m^{-3}	

Refinement

R_p = 0.0602	868 reflections
R_{wp} = 0.0794	31 parameters
R_e = 0.0281	

Table 1. *Fractional atomic coordinates and anisotropic displacement parameters* (Å$^2 \times 10^3$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	Site	x	$y = z$	U_{11}	$U_{22} = U_{33}$	$U_{12} = U_{13}$	U_{23}
Y	16(d)	1/2	1/2	4.51 (6)	$= U_{11}$	−0.97 (7)	$= U_{12}$
Ru	16(c)	0	0	2.33 (7)	$= U_{11}$	0.08 (7)	$= U_{12}$
O1	48(f)	0.33536 (3)	1/8	5.35 (9)	$= U_{11}$	0.0	1.64 (10)
O2	8(b)	3/8	3/8	3.40 (19)	$= U_{11}$	0.0	0.0

Time-of-flight neutron diffraction data were collected on POLARIS at ISIS, Rutherford Appleton Laboratory. The sample (*ca* 5 g) was contained in a vanadium can. The time-of-flight diffraction data from the back-scattering detectors (*C* bank) were analysed by Rietveld profile analysis using the program *GSAS* (Larson & Von Dreele, 1991). The Rietveld refinement was performed on all data points with *d* spacings between 0.325 and 3.2 Å (time-of-flight 2–19.5 ms). Since a number of very weak reflections indicative of Y$_2$O$_3$ were observed in the neutron diffraction pattern, a two-phase refinement was undertaken. Structural parameters for Y$_2$O$_3$ were taken from Faucher & Pannetier (1980).

Atomic positions and anisotropic displacement parameters of the pyrochlore phase were refined simultaneously with the background and profile coefficients. Neutron scattering lengths used were Y 0.7750, Ru 0.7210 and O 0.5805 × 10^{-12} cm (Sears, 1984).

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Structure Refinement of Orthorhombic MnAl₃

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Abstract

Structure refinements on a crystal of composition Mn_3Al_{10} were performed in space groups *Pnma* and *Pn2₁a* (standard setting *Pna2₁*). The space group *Pnma* was found to be correct.

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Comment

The approximate chemical composition and lattice parameters of orthorhombic MnAl₃ were first reported by Hofmann (1938). The phase was found to be stable in the temperature range 1123–1263 K (Taylor, 1960) and to crystallize in space group *Pnma* with 36 Mn and 124 Al atoms per unit cell (Taylor, 1961). A structure model with 156 atoms per unit cell (space group *Pnma*) was proposed by Li, Shi & Kuo (1992), and refined from single-crystal X-ray data by Kang, Malaman, Venturini & Dubois (1992), using a crystal of composition $Al_{61.3}Cu_{7.4}Fe_{11.1}Cr_{17.2}Si_3$, and by Hiraga, Kaneko, Matsuo & Hashimoto (1993), using a crystal of composition $Mn_{3.3}Al_{9.7}$ (found in an ingot prepared by arc melting). Recently, the structure of MnAl₃ was redetermined by Shi, Li, Ma & Kuo (1994) from X-ray diffraction data on a single crystal (found in an ingot prepared by arc melting and annealed at 1223 K for 72 h), and was described with the non-centrosymmetric space group *Pn2₁a* (standard setting *Pna2₁*). At the same time an independent X-ray study of that compound was performed in our laboratories.

Well developed single crystals with orthorhombic symmetry were isolated from a binary alloy containing small amounts of lithium. Structure refinements were performed in centrosymmetric *Pnma* and non-centrosymmetric *Pn2₁a* based on both isotropic and anisotropic displacement amplitudes. For *Pnma*, the results of the anisotropic refinement are summarized in Table 1. For *Pn2₁a*, the anisotropic refinement did not converge, therefore only the results of the isotropic refinements are compared in Table 2. Clearly, the
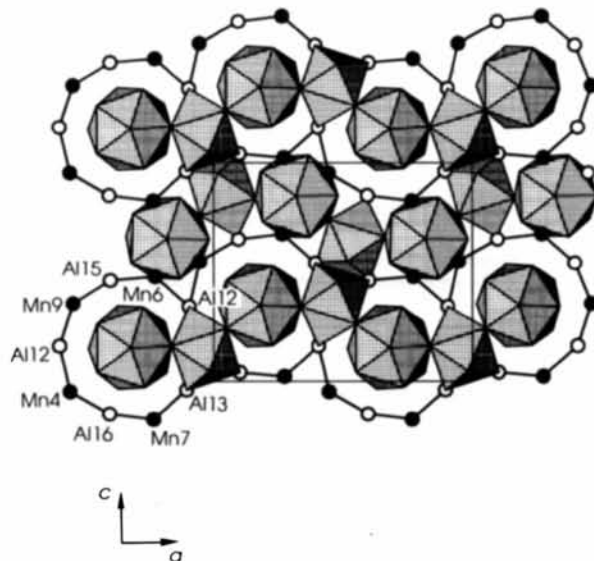

Fig. 1. Structural projection of orthorhombic MnAl₃ along [010], showing the coordination polyhedra of Mn(2) (icosahedra) and Mn(9) (nine-coordinate).