

## ***Ab initio* Structure Determinations of Two Lanthanum Palladium Oxides by Modelling and Powder Diffraction Methods**

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### **Abstract**

Two new structure types,  $\text{La}_2\text{Pd}_2\text{O}_5$  [ $M_r = 570.66$ , tetragonal,  $P4_2/m$ ,  $a = 6.703$  (2),  $c = 5.630$  (2) Å,  $V = 252.96$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 7.49$  g cm<sup>-3</sup>,  $F(000) = 492$ ] and  $\text{La}_4\text{PdO}_7$  [ $M_r = 774.04$ , monoclinic,  $C2/m$ ,  $a = 13.469$  (1),  $b = 4.0262$  (1),  $c = 9.448$  (1) Å,  $\beta = 133.42$  (1)°,  $V = 372.10$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 6.94$  g cm<sup>-3</sup>,  $F(000) = 660$ ], have been solved using a simple modelling technique based on minimum cation–cation distances, and refined with room-temperature powder diffraction data. Least-squares refinement of the structure of  $\text{La}_2\text{Pd}_2\text{O}_5$  using 63 integrated intensities containing contributions from 106 unique reflections leads to  $wR(I) = 4.5\%$ . A Rietveld refinement of  $\text{La}_4\text{PdO}_7$  using time-of-flight neutron diffraction data gives  $R_{\text{nuc}} = 13.0\%$ ,  $R_w = 12.6\%$ ,  $S_p = 1.12$ , for 372 reflections.

### **Introduction**

There is currently much interest in solving crystal structures *ab initio* from powder diffraction data (Lehmann, Christensen, Fjellvag, Feidenhansl & Nielsen, 1987), as modern powder diffractometers can produce well resolved powder patterns with good peak-to-background ratios in acceptable counting times, especially when intense synchrotron X-ray (Cox, Hastings, Cardoso & Finger, 1986; Cox, Hastings, Thomlinson & Prewitt, 1983) or time-of-flight (TOF) neutron sources (Cheetham, 1988) are used. Sufficient reliable  $|F_o|$ 's can be extracted to solve small low-symmetry structures by Patterson techniques, for example, Attfield, Sleight & Cheetham (1986) or direct methods (Cheetham, David, Eddy, Jakeman, Johnson & Torardi, 1986) in many cases, and refinements are performed by Rietveld's (1969) profile method. However, it is extremely difficult to obtain accurate  $|F_o|$ 's for solving cubic or uniaxial structures with low Laue symmetry (Laue groups  $m\bar{3}$ ,  $6/m$ ,  $\bar{3}$ ,  $4/m$ ), as reflections arising from different permutations of the same  $h,k,l$  values have the same  $d$  spacings but unequal  $|F|$ 's (e.g.  $hkl$  and  $khl$  in Laue group  $4/m$ ). There are also some reflections arising from different sets of  $h,k,l$  values that are overlapped in cubic and uniaxial systems (e.g. tetragonal 431 and 501). Extracting

$|F_o|$ 's from powder data may also be difficult if there are accidental relationships between cell parameters, or if significant amounts of crystalline impurities are present in the sample. When some of these problems are encountered, it may not be possible to solve even simple structures from powder data by conventional crystallographic methods requiring  $|F_o|$ 's. In this paper we consider an alternative approach; that of determining the cell parameters and possible space group(s) from the powder pattern, and combining these with geometric information to build up structural models.

From a basic description of metal oxide structures, we have developed a simple technique of modelling cation positions which is used in combination with semiquantitative or quantitative fits to powder diffraction intensities to unravel the structure. This approach has been used to solve the structures of two lanthanum palladium oxides, which typify the previously unknown  $\text{Ln}_2\text{O}_3 \cdot 2\text{PdO}$  and  $2\text{Ln}_2\text{O}_3 \cdot \text{PdO}$  structure types reported in several  $\text{Ln}_2\text{O}_3$ -PdO systems (McDaniel & Schneider, 1968; Kakhan, Lazarev & Shaplygin, 1982*a,b*).

### **Modelling cation positions in metal oxides**

Metal oxide and other ionic structures can be described in several ways. Descriptions in terms of coordination polyhedra emphasize the geometry around the cations, and may be useful in building frameworks from regular polyhedra, for example, silicate structures. However, many cations have variable coordination numbers and irregular coordination polyhedra, and an alternative description of the structure as an arrangement of spherical ions, packed so as to minimize the lattice energy, may be more useful. The balance of all the interactions between the ions tends to result in short nearest-neighbour  $M$ -O distances and large minimum cation–cation distances  $d(M-M)$ , usually  $> 2r(M^{n+})$  unless metal–metal bonding occurs.  $d(M-M)$  depends upon the balance between  $M-M$  repulsions and attractive interactions of the cations with nearby anions. Hence, the cations may be described as spheres of radius  $d(M-M)/2$  which we will assume to be packed in an efficient manner. For simple structures there are probably few cation arrangements that satisfy all  $d(M-M)$  values, and are consistent with the crystal

symmetry and cell dimensions. If the cations account for a large proportion of  $F(000)$ , as often occurs, then comparison of simulated X-ray powder patterns with the observed diffraction intensities can be used to determine which cation arrangement is correct. The O atoms can be located by further modelling, as illustrated later for La<sub>4</sub>PdO<sub>7</sub>, or by crystallographic methods.

The appeal of this simple approach is that only the cation positions are considered. Other techniques such as packing arguments, distance least-squares calculations or lattice-energy minimization require both cation and anion positions, and hence a more detailed structural model.

In this work we have attempted to model cation arrangements that satisfy the above criteria by restrained least-squares refinements of arbitrary starting models. A commonly used function for restraining an interatomic distance ( $r$ ) during weighted least-squares refinement is

$$D(r) = (1/\sigma^2)(r-r_0)^2,$$

where  $r_0$  is the target distance and  $\sigma$  is the e.s.d. of  $r_0$  (Rollett, 1969). This acts as a crude approximation to a bonding potential, and so is appropriate when the topology of a structure is already known, as during the final stages of a refinement (Hendrickson & Konnert, 1980), but is inappropriate for generating structures when only a limiting minimum distance between all pairs of atoms is known. Instead a hard-sphere-like potential is required, and we use the function

$$E(r) = (r_0/r)^{12}(r-r_0)^2,$$

where  $r_0$  is set to the assumed value for  $d(M-M)$  (Watkin, 1988). By choosing arbitrary cation positions, setting up  $E$  restraints between all cations within a large radius ( $\sim 7$  Å) of each cation in the unit cell, and performing a restrained full-matrix least-squares refinement of the coordinates, plausible cation arrangements can easily be generated. The positions adopted by the cations are dependent upon the initial configuration, and so the operation may need to be repeated several times with different starting models to find all possible sets of cation positions. It is also necessary to choose the symmetry positions of the cations, so different combinations of positions may have to be tried to generate the correct model.

The interactive program *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985) was used to generate the restraints and refine the starting model, enabling trial cation arrangements to be obtained quickly. Simulated X-ray powder patterns were produced with *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977) and integrated intensity refinements were performed with Wiseman's (1974) program. A program employing CCSL subroutines (Brown & Matthewman, 1987) was used for the TOF neutron profile refinements.

## Experimental

Polycrystalline La<sub>2</sub>Pd<sub>2</sub>O<sub>5</sub> was prepared by adding appropriate quantities of La<sub>2</sub>O<sub>3</sub> and PdO to concentrated nitric acid, heating the mixture to dryness, and firing the residue at 1343 K in air for a week. La<sub>4</sub>PdO<sub>7</sub> was prepared by firing a well ground mixture of La<sub>2</sub>O<sub>3</sub> and PdO in a 2:1 ratio at 1353 K. The product contained traces of La<sub>2</sub>O<sub>3</sub> and was reheated with small additions of PdO until the impurity was no longer evident in the X-ray diffraction pattern of the material.

X-ray diffraction data were collected on an automated Philips PW 1710 powder diffractometer using nickel-filtered Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å). The sample was placed in a shallow aluminium tray, and the reflected diffraction pattern was recorded by a xenon-filled proportional detector.

The TOF neutron data for La<sub>4</sub>PdO<sub>7</sub> were collected by the High Resolution Powder Diffractometer (HRPD) on the Spallation Neutron Source ISIS at the Rutherford-Appleton Laboratory, which employs a 95 m primary neutron flight path and backscattering geometry to produce highly resolved diffraction data. More details are given by Johnson & David (1985).\*

## Structure determinations

### (i) La<sub>2</sub>Pd<sub>2</sub>O<sub>5</sub>

X-ray data were collected from 10 to 90°  $2\theta$  in 0.05° steps, counting for 4 s per step. All of the observed peaks could be indexed on the reported tetragonal cell (Kakhan, Lazarev & Shaplygin, 1982a) and the parameters  $a$  and  $c$  were obtained from a refinement using 26 reflection positions. The only observed reflection condition was  $00l$ ,  $l = 2n$ , indicative of space groups  $P4_222$ ,  $P4_2/m$  and  $P4_2$ .  $Z = 2$  gives a reasonable value of 7.49 g cm<sup>-3</sup> for  $D_x$ .

57 integrated reflection intensities were obtained manually and converted to  $|F_0|^2$ 's, assuming  $4/mmm$  Laue symmetry. These were used to construct a Patterson map that contained high density in the  $(u,v,0)$  and  $(u,v,\frac{1}{2})$  planes, but no Harker peaks at  $(0,0,\frac{1}{2})$  or  $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ . This could not be interpreted in  $P4_222$ , suggesting that all the heavy atoms lie in the  $(x,y,0)$  plane in  $P4_2/m$ , or have approximately equal  $z$  values in  $P4_2$ . The cation positions could not be determined directly from the Patterson map as  $P4_2/m$  and  $P4_2$  have  $4/m$  Laue symmetry, and so we attempted to model the cation positions.

\* Time-of-flight data for La<sub>4</sub>PdO<sub>7</sub> (as microfiche), lists of structure factors for La<sub>2</sub>Pd<sub>2</sub>O<sub>5</sub> and all bond lengths and angles for both compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51160 (10 pp. and 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

La and Pd atoms were placed at arbitrary positions in the  $(x,y,0)$  plane and  $E$  restraints were set up with  $r_0$  values of 3.7, 3.3 and 2.8 Å for La–La, La–Pd and Pd–Pd contacts, respectively, based on the minimum cation–cation distances in several lanthanum and palladium oxides. Refinement of the four variable coordinates in  $P4_2/m$  led to a stable solution with the coordinates shown in Table 1. The simulated X-ray powder intensities appeared very similar to the observed pattern, showing that these positions were approximately correct.

O-atom positions were found by inspection and the structure was refined in  $P4_2/m$  using 63 composite integrated intensities from 106 unique reflections as observations. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974), and no anomalous-dispersion corrections were made. The results of the refinement are shown in Table 1 and bond distances and angles are given in Table 2.

### (ii) $\text{La}_4\text{PdO}_7$

The X-ray pattern of our sample agreed with that reported for  $\text{La}_4\text{PdO}_7$  (Kakhan, Lazarev & Shaplygin, 1982*a*), but the peak positions were not sufficiently precise for the unit cell to be determined. In order to obtain more highly resolved diffraction peaks, TOF neutron diffraction profiles were recorded on HRPD at room temperature. Data were collected in 30–130 and 90–190 ms frames, corresponding to  $d$ -space ranges of 0.6–2.7 and 1.9–3.9 Å, respectively. The 39 highest TOF peak positions were input into Visser's (1969) program, which indexed all the reflections on a  $C$ -centred monoclinic cell [ $a = 13.471$  (2),  $b = 4.027$  (1),  $c = 9.446$  (2) Å,  $\beta = 133.42$  (3)°]. Assuming  $Z = 2$  gives a reasonable density;  $D_x = 6.94$  g cm<sup>-3</sup>. Only the reflection condition due to  $C$  centring was observed in the X-ray and neutron diffraction patterns of  $\text{La}_4\text{PdO}_7$ , giving  $C2/m$ ,  $Cm$  and  $C2$  as possible space groups.

Although the monoclinic symmetry of this material makes structure determination from powder data by conventional crystallographic methods feasible, we attempted to solve the structure using only the modelling technique described above. In view of the short  $b$ -axis length, the most likely space-group choices seemed to be  $C2/m$ , with atoms lying on the mirror planes at  $(x,0,z)$  and  $(x,\frac{1}{2},z)$ , or  $C2$ . We initially modelled the structure in  $C2/m$ . Pd was placed at (0,0,0), and two independent La atoms were placed arbitrarily in the  $(x,0,z)$  plane. La–La and La–Pd restraints were set up as before using  $r_0$  values from the  $d(M-M)$  values in  $\text{La}_2\text{Pd}_5\text{O}_5$ . Several refined cation arrangements were produced from different starting configurations, only one of which gave a simulated diffraction pattern that bore some resemblance to the actual X-ray intensities. In order to improve this model,

Table 1. Results of the refinement of the structure of  $\text{La}_2\text{Pd}_2\text{O}_5$  in  $P4_2/m$  with e.s.d.'s in parentheses

Variable coordinates for the modelled cation positions (marked  $M$ ) are also given.

Number of observed integrated intensities	63			
Number of unique reflections	106			
Maximum $(\sin\theta)/\lambda$ (Å <sup>-1</sup> )	0.46			
Number of refined parameters	9			
Maximum (shift/e.s.d.)	0.0009 on O(1): z			
$wR(I)^*$	4.5%			
Symmetry				
	position	$x$	$y$	$z$
La	4( $j$ )	0.2648 (4)	0.1080 (6)	0
		0.25 (1) $M$	0.12 (1) $M$	
Pd	4( $j$ )	0.3099 (6)	0.5951 (6)	0
		0.33 (1) $M$	0.61 (1) $M$	
O(1)	8( $k$ )	0.198 (3)	0.402 (3)	0.255 (3)
O(2)	2( $e$ )	0	0	$\frac{1}{4}$

Overall  $B_{\text{iso}} = -0.10$  (6) Å<sup>2</sup>

$$* wR(I) = [\sum w(I_o - I_c)^2 / \sum wI_o^2]^{1/2} \text{ where } w = 1/\sigma(I_o)^2.$$

Table 2. Selected distances (Å) and angles (°) in  $\text{La}_2\text{Pd}_2\text{O}_5$  (e.s.d.'s in parentheses)

Bond lengths					
La–O(1)	(×2)	2.48 (2)	Pd–O(1 <sup>iii</sup> )	(×2)	2.05 (2)
La–O(1 <sup>i</sup> )	(×2)	2.64 (2)	Pd–O(1)	(×2)	2.07 (2)
La–O(1 <sup>ii</sup> )	(×2)	2.69 (2)			
La–O(2)	(×2)	2.378 (2)			
Short $M-M$ and O–O distances					
La...La <sup>iv</sup>		3.470 (6)	Pd...Pd <sup>iv</sup>		2.850 (8)
La...La <sup>v</sup>		3.834 (6)	Pd...Pd <sup>vi</sup>	(×4)	3.462 (3)
La...La <sup>i</sup>	(×4)	3.908 (3)	O(1)...O(1 <sup>iii</sup> )		2.76 (3)
La...Pd <sup>vi</sup>	(×2)	3.261 (3)	O(1)...O(1 <sup>ii</sup> )		2.87 (3)
La...Pd		3.279 (6)	O(2)...O(2 <sup>a</sup> )	(×2)	2.815 (1)
La...Pd <sup>iii</sup>		3.477 (5)			
Angles around Pd					
O(1 <sup>iii</sup> )–Pd–O(1 <sup>ii</sup> )		84 (1)	O(1 <sup>iii</sup> )–Pd–O(1 <sup>ii</sup> )		93.7 (5)
O(1)–Pd–O(1 <sup>ii</sup> )		88 (1)	O(1)–Pd–O(1 <sup>ii</sup> )		175.3 (8)

Symmetry code: (i)  $y, -x, -\frac{1}{2}+z$ ; (ii)  $1-y, x, \frac{1}{2}-z$ ; (iii)  $y, 1-x, \frac{1}{2}-z$ ; (iv)  $1-x, -y, z$ ; (v)  $-x, -y, z$ ; (vi)  $1-y, x, \frac{1}{2}+z$ ; (vii)  $1-x, 1-y, z$ ; (viii)  $x, y, 1-z$ ; (ix)  $x, y, -z$ ; (x)  $-y, x, \frac{1}{2}+z$ ; (xi)  $x, 1-y, -\frac{1}{2}+z$ .

and to determine whether the space group was  $C2/m$  or  $C2$ , the cation positions were refined in both groups using 48 X-ray peak heights from a routine diffraction profile as observations. The best fit with  $wR(I) = 27\%$  was obtained in  $C2$  and so further development of the structure was performed in this space group. The cation positions are shown in Table 3.

Sections of the cell parallel to (010) were constructed at several values of  $y$ , and circles with radii equivalent to Pd–O and La–O bond distances of 2.0 and 2.4 Å were drawn around the projected cation positions. Possible O-atom sites were located at the intersections of two or more spheres provided no short  $M-O$  contacts resulted. Seven positions corresponding to 22 O-atom sites per cell were found and their coordinates were improved by further modelling of the structure in order to optimize the  $M-O$  distances.  $D$

Table 3. Trial model for La<sub>4</sub>PdO<sub>7</sub> in C2 with e.s.d.'s in parentheses

The cation positions were modelled using *E*-type restraints on metal-metal distances and fixed during the restrained refinement of the O-atom positions.

	Symmetry position	x	y	z
La(1)	4(c)	0.255 (7)	0.48 (1)	0.170 (9)
La(2)	4(c)	0.604 (5)	-0.11 (1)	0.379 (9)
Pd	2(a)	0	0	0
O(1)	2(a)	0	0.50 (2)	0
O(2)	4(c)	0.35 (1)	-0.02 (2)	0.17 (1)
O(3)	4(c)	0.09 (1)	0.00 (2)	-0.10 (2)
O(4)	4(c)	0.32 (1)	0.40 (2)	0.47 (2)
O(5)	2(b)	0	0.25 (2)	$\frac{1}{2}$
O(6)	2(b)	0	0.75 (2)	$\frac{1}{2}$
O(7)	4(c)	0.19 (2)	-0.02 (2)	0.25 (1)

restraints were set up for Pd-O bonds ( $r_0 = 2.0 \text{ \AA}$ ) but *E* restraints ( $r_0 = 2.4 \text{ \AA}$ ) were used for La-O distances to allow for the large variation of La-O bond lengths that may be observed in the coordination sphere of La<sup>3+</sup>. The cation positions were fixed and the O-atom coordinates were refined to the values shown in Table 3.

Final development of this structure was performed by profile fits to the 30-130 ms set of neutron data. The coordinates in Table 3 were used as a starting model in C2, with all of the O-atom sites half occupied. Neutron scattering lengths were taken from Bacon (1975). After fitting the profile parameters, the O-atom occupancy factors were refined; the results indicated that the O(5)-O(7) sites were unoccupied and these positions were omitted from future refinements. The occupation factors of the remaining O atoms were fixed at 1.0, and the coordinates of all the atoms were varied. The refinement converged to an unstable minimum and the varied *y* values oscillated around  $y = 0$  or  $\frac{1}{2}$ , suggesting that the structure has C2/*m* symmetry. A stable refinement giving a good fit to the data was obtained in C2/*m* after several diffraction peaks due to traces of Pd and La<sub>2</sub>O<sub>3</sub> had been excluded from the calculations. The results are given in Table 4 and bond distances and angles are shown in Table 5. Observed, calculated and difference profiles are displayed in Fig. 1.

### Crystal structures

Projections of the crystal structures of La<sub>2</sub>Pd<sub>2</sub>O<sub>5</sub> and La<sub>4</sub>PdO<sub>7</sub> are shown in Figs. 2 and 3. In La<sub>2</sub>Pd<sub>2</sub>O<sub>5</sub>, pairs of square-planar PdO<sub>4</sub> units form infinite double chains (Fig. 4) parallel to **c**, and eight-coordinate La<sup>3+</sup> lie between the chains. La<sub>4</sub>PdO<sub>7</sub> contains isolated linear chains of apically linked PdO<sub>4</sub> units parallel to **b** and seven- and eight-coordinate La<sup>3+</sup> cations. The bond distances and angles in Tables 2 and 5 are comparable with those in other lanthanum and palladium oxides. Fuller descriptions of these novel structures and their relationships with other structure types will be published elsewhere (Attfield & Ferey, 1988).

Table 4. Results of the Rietveld refinement of La<sub>4</sub>PdO<sub>7</sub> in C2/*m* using neutron diffraction data, with e.s.d.'s in parentheses

Number of profile points ( <i>N</i> )	7219		
Number of unique reflections	372		
(sin $\theta$ )/ $\lambda$ range ( $\text{\AA}^{-1}$ )	0.19-0.83		
Number of refined parameters ( <i>P</i> )	28		
Maximum (atomic parameter shift/e.s.d.)	0.002 on <i>B</i> <sub>iso</sub> (Pd)		
<i>R</i> factors (%)*	<i>R</i> <sub>p</sub> = 9.9	<i>R</i> <sub>nuc</sub> = 13.3	<i>R</i> <sub>ex</sub> = 11.3
<i>R</i> <sub>wp</sub> = 12.6			
<i>S</i> <sub>p</sub> † = 1.12			
Cell constants ( $\text{\AA}$ , °)			
<i>a</i> = 13.469 (1)	<i>b</i> = 4.0262 (1)	<i>c</i> = 9.448 (1)	$\beta$ = 133.42 (1)
Peak-width parameter‡ <i>s</i> = 378 (3) $\mu$ s			

	Symmetry position	x	y	z	<i>B</i> <sub>iso</sub> ( $\text{\AA}^2$ )
La(1)	4( <i>i</i> )	0.2470 (3)	$\frac{1}{2}$	0.1540 (4)	0.40 (6)
La(2)	4( <i>i</i> )	0.5839 (3)	0	0.3889 (5)	0.13 (5)
Pd	2( <i>a</i> )	0	0	0	0.08 (9)
O(1)	2( <i>b</i> )	0	$\frac{1}{2}$	0	3.8 (2)
O(2)	4( <i>i</i> )	0.3673 (4)	0	0.3101 (6)	0.47 (8)
O(3)	4( <i>i</i> )	0.0875 (5)	0	-0.1126 (8)	1.49 (7)
O(4)	4( <i>i</i> )	0.2961 (5)	$\frac{1}{2}$	0.4462 (7)	1.51 (9)

\* The profile *R* factors are defined by Rietveld (1969).

†  $S_p = [\sum w(y_o - y_c)^2 / (N - P)]^{1/2}$ .

‡ The Gaussian (sample-broadened) part of the peak shape was fitted using  $\sigma^2 = s\lambda^2$ , where  $\lambda$  is the neutron wavelength at the peak TOF and  $\sigma^2$  is the second moment of the Gaussian. The instrumental part is described by Johnson & David (1985).

Table 5. Selected distances ( $\text{\AA}$ ) and angles (°) in La<sub>4</sub>PdO<sub>7</sub> with e.s.d.'s in parentheses

Bond lengths			
La(1)-O(1)	2.555 (4)	La(2)-O(2)	2.466 (7)
La(1)-O(2) (x2)	2.360 (2)	La(2)-O(3 <sup>ii</sup> ) (x2)	2.813 (5)
La(1)-O(3 <sup>i</sup> )	2.51 (1)	La(2)-O(4 <sup>iii</sup> ) (x2)	2.373 (3)
La(1)-O(3) (x2)	2.752 (4)	La(2)-O(4 <sup>iv</sup> )	2.517 (9)
La(1)-O(4)	2.355 (8)	Pd-O(1) (x2)	2.0131 (1)
La(2)-O(1 <sup>ii</sup> )	3.011 (5)	Pd-O(3) (x2)	2.060 (9)
La(2)-O(2 <sup>iii</sup> )	2.439 (8)		
Short <i>M-M</i> and O-O distances			
La(1)⋯La(1 <sup>i</sup> ) (x2)	3.585 (7)	La(2)⋯La(2 <sup>ii</sup> ) (x2)	3.945 (7)
La(1)⋯La(2 <sup>iii</sup> ) (x2)	3.791 (5)	La(2)⋯Pd <sup>iv</sup> (x2)	3.622 (4)
La(1)⋯La(2 <sup>i</sup> )	3.840 (8)	O(1)⋯O(3) (x4)	2.880 (7)
La(1)⋯La(2) (x2)	3.966 (5)	O(2)⋯O(2 <sup>iii</sup> )	2.832 (8)
La(1)⋯Pd (x2)	3.253 (3)	O(2)⋯O(4) (x2)	2.884 (8)
Angles around Pd			
O(1)-Pd-O(1 <sup>v</sup> )	180	O(3)-Pd-O(3 <sup>vi</sup> )	180
O(1)-Pd-O(3)	90		

Symmetry code: (i)  $\frac{1}{2}-x, \frac{1}{2}+y, -z$ ; (ii)  $\frac{1}{2}+x, -\frac{1}{2}+y, z$ ; (iii)  $1-x, y, 1-z$ ; (iv)  $\frac{3}{2}-x, \frac{1}{2}+y, 1-z$ ; (v)  $x, 1-y, z$ ; (vi)  $-x, y, -z$ .

### Discussion

These two structure determinations illustrate the use of modelling as an alternative or aid to conventional crystallographic methods. This approach might also be useful in modelling structures containing coordination complexes, small molecules, or any fairly rigid approximately spherical group, although the orientation would also have to be determined.

$\text{La}_2\text{Pd}_2\text{O}_5$  has a very simple structure, enabling the cation positions to be modelled to within 0.2 Å of their refined positions. This discrepancy is equal to the difference between the minimum La–La distance of 3.5 Å and our assumed value of 3.7 Å for  $d(\text{La}–\text{La})$ . Although the precision of the final refinement using X-ray powder data is low, it does confirm the structure and provide a description that is sufficient for most purposes.

The modelled La positions (Table 3) for  $\text{La}_4\text{PdO}_7$  are up to 0.5 Å from their final refined positions, due in part to the model having been developed in  $C2$  instead of  $C2/m$ . However, the model is sufficiently close to the actual structure for the profile refinements to have been straightforward. Although there are discrepancies in the fits to some of the most intense peaks (see Fig. 1), perhaps due to an inadequate peak-shape description, the overall fit is good and the precision on the refined atomic coordinates approaches that of single-crystal X-ray studies. Our structure determination of  $\text{La}_4\text{PdO}_7$  also illustrates the complementarity of X-ray and neutron methods in solving heavy-atom structures by powder methods. X-ray data are preferable for finding the heavy-atom positions by modelling or crystallographic methods, while structure refinement using

neutron data allows the light atoms to be located precisely. A simultaneous structure refinement with X-ray and neutron profiles (Maichle, Ihringer & Prandl, 1988) could be used to combine the advantages of the two techniques.

The success of this cation modelling technique depends upon there being a high density of cations in the structure, rather than knowledge of accurate cation–cation distances. The cation density may be quantified by using the effective radii [ $=d(M–M)/2$ ] which are 1.5–2.0 times greater than the ionic radii of these cations (Shannon, 1976). Our effective spheres of radii 1.75 Å for  $\text{La}^{3+}$  and 1.40 Å for  $\text{Pd}^{2+}$  occupy 54% of the cell volume in both materials. Although this density is not necessarily high enough to result in efficient sphere packings, the constraints imposed by the lattice parameters and symmetry operators enabled

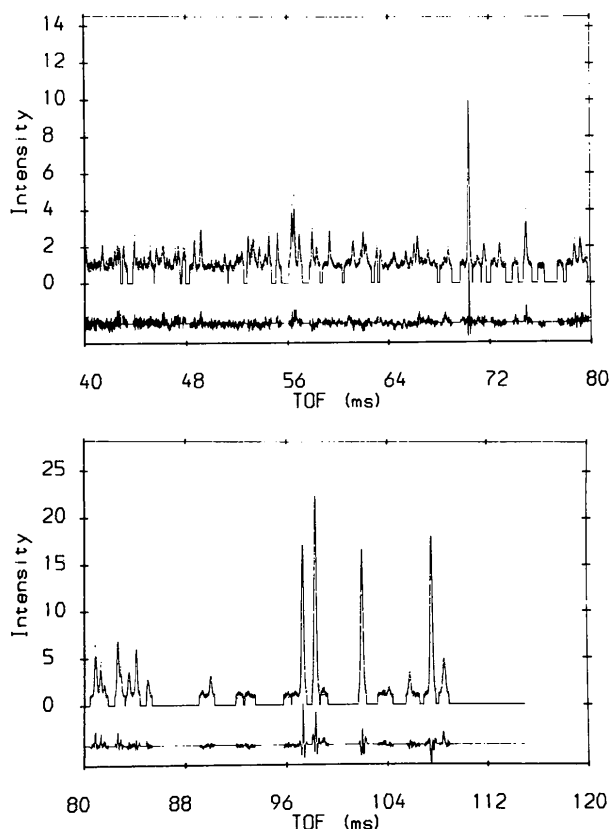


Fig. 1. Observed (points), calculated (full line) and difference TOF neutron diffraction profiles for  $\text{La}_4\text{PdO}_7$ . The intensities are in neutrons  $\text{ms}^{-1}$ .

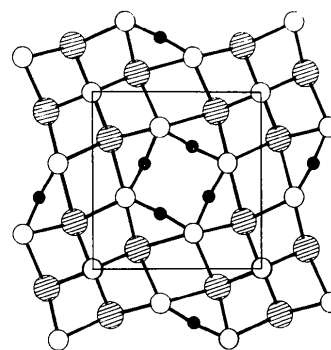


Fig. 2. The crystal structure of tetragonal  $\text{La}_2\text{Pd}_2\text{O}_5$  projected on (001). (La, large hatched circles; Pd, small shaded circles; O, medium open circles.)

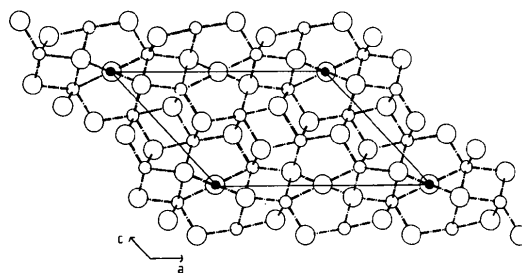


Fig. 3. A view of the  $ac$  plane of monoclinic  $\text{La}_4\text{PdO}_7$ . (La, small open circles; Pd, small shaded circles; O, large open circles.)

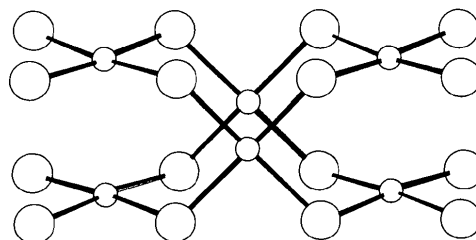


Fig. 4. The double chain of  $\text{PdO}_4$  units that runs parallel to  $c$  (the horizontal direction) in  $\text{La}_2\text{Pd}_2\text{O}_5$ .

stable cation arrangements to be produced in both cases. Tables 2 and 5 show that there are few cation–cation distances comparable to the  $d(M-M)$  values used in the restrained refinements of the starting models. Although O<sup>2-</sup> has a greater ionic radius than La<sup>3+</sup> or Pd<sup>2+</sup>, the minimum O–O distance in these materials is less than the smallest cation–cation distance, reflecting the greater polarizability of the anion. Thus, it is more useful to consider cation–cation distances than anion–anion contacts in attempting to model such structures.

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## Examination of $n$ -Beam Interaction: X-ray Experiment and Simulation for KMnF<sub>3</sub>

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#### Abstract

The intensity equation of the  $n$ -beam interaction based on the kinematical theory [Soejima, Okazaki & Matsumoto (1985). *Acta Cryst.* **A41**, 128–133] is examined for the case of X-ray diffraction in KMnF<sub>3</sub>. With

a few examples of the fundamental and superlattice diffractions, it is shown that the equation reproduces the experimental  $\psi$ -scan patterns which result from  $n$ -beam interaction. The spectral width of the incident beams is the main contribution to the thickness of the Ewald sphere, and is taken into account. It is confirmed that the  $\psi$ -scan patterns are sensitive to the symmetry of the crystal structure: the patterns must be and are identical for symmetry-equivalent reflections, and vary at the structural phase transition with a change in symmetry.

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