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The orthorhombic and rhombohedral phases of LaGaO₃—a neutron powder diffraction study

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Abstract. Neutron powder diffraction has been used to examine the crystal structure of the perovskite LaGaO₃, at room temperature, and then at elevated temperatures to 1673 K. The orthorhombic structure at room temperature (*Pbnm*, $a = 5.5245(1)$ Å, $b = 5.4922(1)$ Å, $c = 7.7740(2)$ Å) was confirmed. At temperatures from about 420 K the structure is rhombohedral, in space group $R\bar{3}c$. The rhombohedral structure is characterized by rotation of the oxygen-atom octahedra about the threefold axis, and compression of these octahedra parallel to the same axis. The rotation angle varies from 11.0 to 9.3°, and the octahedral strain parameter (a measure of the compression) from 0.969 to 0.983 over the temperature range of this study. The question as to whether the two effects are coupled is considered but not yet resolved.

1. Introduction

As part of current systematic investigations of compounds of the perovskite family, with particular emphasis on crystal structures and phase transitions [1–5], we have re-examined the crystal structure of LaGaO₃ and its evolution with temperature in the range from room temperature (295 K) to 1673 K. Perovskite LaGaO₃ has been shown to be orthorhombic in space group *Pbnm* at ambient temperature [6, 7], and to undergo a first-order transition to a rhombohedral space group at 418 K [8]. In his early study, based on differential thermal analysis, Geller [6] put the phase transition at a considerably higher temperature, 1150 K, but recent studies [7–10] are in agreement on the lower transition temperature. Marti *et al* [7] gave the space group of the rhombohedral structure as *R3c*. Most of the recent studies of LaGaO₃ have been motivated by its possible use as a substrate for epitaxial high-temperature superconducting thin films [9].

Recently, as part of our own programme on perovskites, we have completed three detailed neutron powder diffraction studies [3–5] of the tetragonal perovskite structure ($a^0a^0c^-$ in Glazer's notation [11]) as a function of temperature, and our main interest here was to undertake a similar study of a perovskite with the rhombohedral structure ($a^-a^-a^-$ in Glazer's notation). The lattice parameter data for LaGaO₃ [8] are taken to indicate that the material will retain the rhombohedral structure to temperatures above the melting point (~ 2000 K), and in studies to 1673 K Marti *et al* [7] reported only the one phase transition, that to the rhombohedral phase. Nonetheless, the crystallographic data presented by Marti *et al* include dramatic

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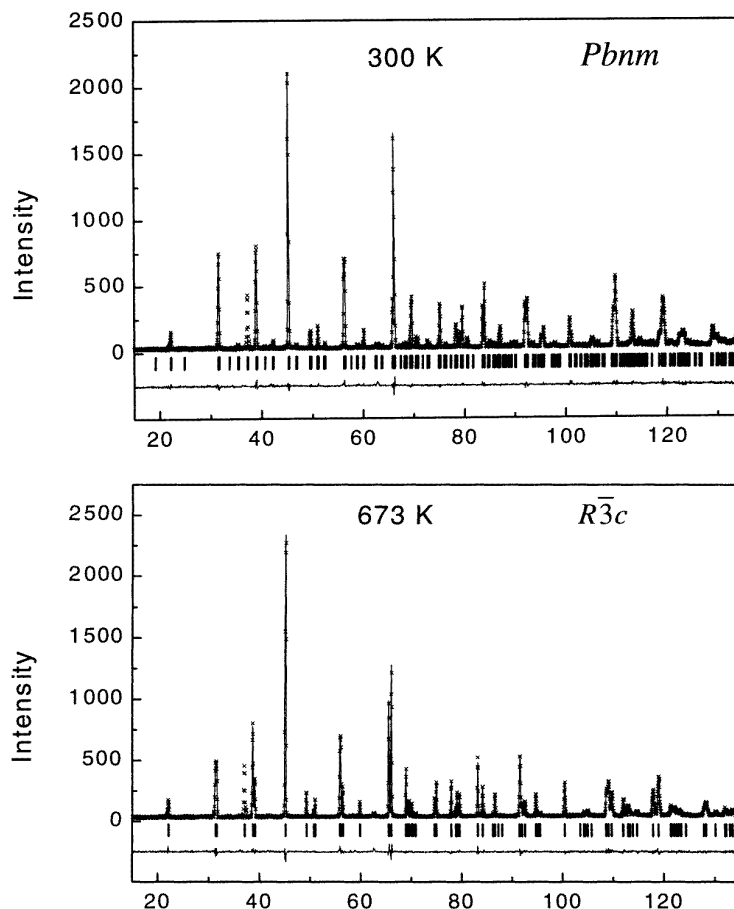


Figure 1. Neutron diffraction patterns ($\lambda = 1.500 \text{ \AA}$) obtained from LaGaO_3 at selected temperatures, with the results of fitting by the Rietveld method. The crosses are the observed data, the continuous curves through these are the patterns calculated after least-squares fitting of the appropriate crystal structures, and the continuous trace under each pattern shows the difference between observed and calculated patterns. Positions of Bragg peaks are marked. The peak seen near 38° is the 110 peak from the Nb heating element, and has been excluded from the refinement in every case. For the fit at 300 K, the measures of fit are $R_p = 5.8\%$, $R_{wp} = 7.8\%$ ($R_{exp} = 6.7\%$), and $R_B = 2.0\%$, for that at 673 K, $R_p = 6.1\%$, $R_{wp} = 7.9\%$ ($R_{exp} = 6.7\%$), and $R_B = 1.9\%$, and for that at 1373 K, $R_p = 6.0\%$, $R_{wp} = 7.6\%$ ($R_{exp} = 6.7\%$), and $R_B = 2.2\%$.

changes in atomic coordinates between 1353 K and 1673 K, and show a lattice at 1673 K which is 'metrically cubic'. Here we report a neutron powder diffraction study of LaGaO_3 to 1673 K, the temperature range of our work being limited by the onset of chemical reaction or decomposition at these high temperatures.

2. Experimental procedure and data analysis

The LaGaO_3 was prepared by the solid-state reaction of stoichiometric amounts of La_2O_3 (Aldrich 99.9%) and Ga_2O_3 (Aldrich 99.99%) at 1173 K in air for 24 hours, and then, after re-grinding, at 1373 K for 48 hours. After a final re-grinding, the sample was annealed at

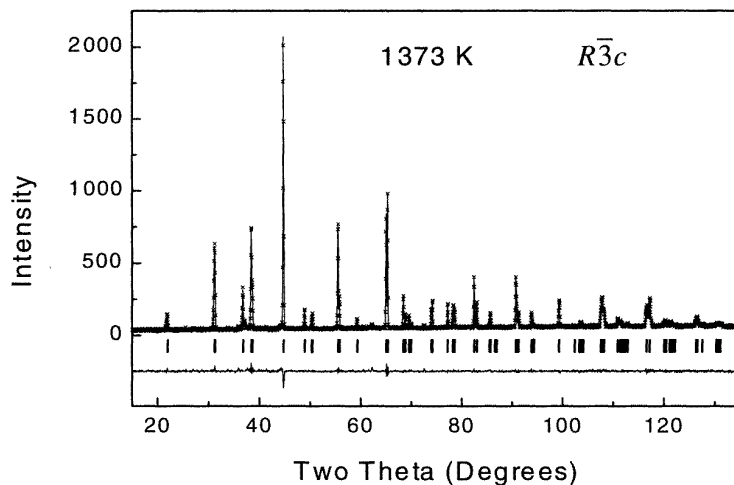


Figure 1. (Continued)

1623 K for 24 h. As far as could be determined by x-ray powder diffraction the sample was single phase. For the neutron diffraction measurements, about 20 g of the powder were loaded into a thin-walled, 13 mm diameter, vanadium sample can, then mounted in an ILL-type vacuum furnace. That furnace was mounted in turn on the neutron powder diffractometer on beam port HB4 at the High Flux Isotope Reactor, Oak Ridge National Laboratory [12]. Diffraction patterns were recorded, using neutrons of wavelength 1.500 Å, over the 2θ range from 11 to 135°, with a step size of 0.05°. Patterns were collected first at room temperature and then at successively higher temperatures, to a maximum of 1673 K. The furnace was pumped throughout the experiment, maintaining a vacuum of about 10^{-6} Torr. The crystal structures were refined by the Rietveld method, using the program LHPM [13] operating on a PC. The background was taken to be a quadratic function of 2θ , and was refined simultaneously with the unit-cell, zero-point, scale, peak width/shape/asymmetry, and crystal structure parameters. The peak profile was described by a Voigt function, in which the widths of the Gaussian and Lorentzian components were coded to vary in accordance with the Caglioti–Paoletti–Ricci function [14] to describe instrumental resolution and strain broadening, and with $\sec\theta$ to describe crystallite size broadening, respectively. The 2θ region near 38° affected by a peak from the furnace heating element was excluded from the refinements.

3. Results

3.1. The orthorhombic structure

The pattern recorded at room temperature was fitted assuming, as previous authors had [6, 7], a structure in $Pbnm$. The well resolved splitting of the 404–044 pair at just under 84° confirms the space group choice [4]. The pattern and fit are shown in figure 1, and the corresponding crystal structure parameters are recorded in table 1. The lattice parameters are in good agreement with those previously reported for this phase [6–8]. The coordinates included in table 1 have been chosen to conform with those shown in our previous studies of perovskites in $Pbnm$ [3–5], but these coordinates cannot be compared directly with those given by Marti *et al* [7]. We find an entirely equivalent fit by placing Ga at $\frac{1}{2}, 0, 0$, and for the other atoms replacing x by $-x$

Table 1. Structures and structural parameters for LaGaO₃ at selected temperatures.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
300 K, <i>Pbnm</i> , <i>a</i> = 5.5245(1) Å, <i>b</i> = 5.4922(1) Å, <i>c</i> = 7.7740(2) Å					
La	4c	0.0041(3)	0.5168(3)	$\frac{1}{4}$	0.36(2)
Ga	4a	0	0	0	0.19(2)
O1	4c	-0.0669(3)	-0.0058(4)	$\frac{1}{4}$	0.41(3)
O2	8d	0.2299(3)	0.2704(3)	0.0356(2)	0.54(3)
673 K, $R\bar{3}c$, <i>a</i> = 5.5429(1) Å, <i>c</i> = 13.4328(2) Å					
La	6a	0	0	$\frac{1}{4}$	0.86(4)
Ga	6b	0	0	0	0.50(4)
O	18e	0.5548(2)	0	$\frac{1}{4}$	1.18(4)
1373 K, $R\bar{3}c$, <i>a</i> = 5.5777(1) Å, <i>c</i> = 13.5806(3) Å					
La	6a	0	0	$\frac{1}{4}$	1.87(6)
Ga	6b	0	0	0	1.29(6)
O	18e	0.5497(3)	0	$\frac{1}{4}$	2.61(6)

and *y* by $\frac{1}{2} - y$. By this means we see that our structure is indeed in excellent agreement with that described by Marti *et al.*

3.2. The rhombohedral structure

All of the patterns recorded above room temperature, that is patterns recorded at 383 K, 673 K, 973 K, 1123 K, 1273 K, 1373 K, 1473 K, 1573 K, and 1673 K, could be fitted assuming a rhombohedral structure, in space group $R\bar{3}c$. Given that the transition to rhombohedral has been reported to occur at 418 K, the appearance of a rhombohedral structure at 383 K was somewhat surprising. This is thought to be due to problems of temperature calibration, probably related to our operation of the high-temperature ILL furnace below its normal range. The patterns recorded at 673 K and 1373 K and the fits obtained are shown in figure 1, and the corresponding parameters are recorded in table 1. Anisotropic thermal parameters appropriate to the different site symmetries were refined but, for brevity, only the equivalent isotropic thermal parameters have been given in the table. Refinements in the non-centrosymmetric space group $R3c$, as assumed by Marti *et al.*, produced neither visible nor measurable improvement in the fit, even though this meant four variable position parameters compared with the one for $R\bar{3}c$. The present authors are not aware of any evidence (e.g. reports of ferroelectric behaviour of LaGaO₃) precluding the use of the centrosymmetric space group. Furthermore, it can be concluded from an examination of the *c/a* ratios (see later) that the oxygen octahedra are compressed along the (hexagonal) *c*-axis, making it unlikely that the Ga cations within these octahedra would be displaced along this axis from the central positions [15]. Accordingly, space group $R\bar{3}c$ was assumed for all refinements of the rhombohedral structure.

Close inspection of the pattern recorded at 1473 K revealed some weak features around 38° in 2θ , which did not appear in patterns recorded at lower temperatures, and were not accounted for by our structural model. These were attributed to some chemical decomposition of the sample, or reaction with the sample can. The unaccounted for features became more prominent at higher temperature, and at 1673 K had developed to the extent that we did not continue to higher temperatures. We believe, however, that they have no significant influence on the parameters derived from our Rietveld fits.

The lattice parameter results over the temperature range 383–1673 K are shown in figure 2.

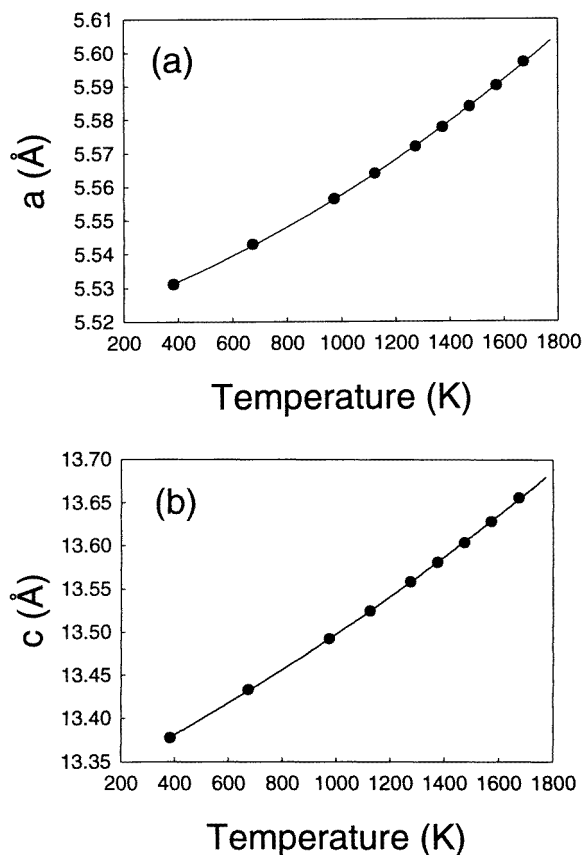


Figure 2. Temperature dependences of the (hexagonal) lattice parameters of LaGaO_3 in its rhombohedral phase. The results for the a - and c -parameters are shown in parts (a) and (b) respectively. The continuous curves in (a) and (b) are the quadratic fits $a = 5.5275[1 + 5.89 \times 10^{-6}(T - 273) + 2.2 \times 10^{-9}(T - 273)^2]$ Å and $c = 13.3595[1 + 12.6 \times 10^{-6}(T - 273) + 2.2 \times 10^{-9}(T - 273)^2]$ Å respectively.

The parameters vary smoothly over the entire temperature range, up to the highest temperature of our measurements. The temperature variation of each lattice parameter is well described by a quadratic function. Marti *et al* [7] used different furnaces over the temperature range of their measurements, and their data are less well behaved; in particular their lattice parameters are apparently higher at 1673 K than a smooth variation would suggest. The ratio $c/(a\sqrt{6})$ from our data is 0.989 at 673 K, 0.994 at 1373 K and 0.996 at 1673 K, whereas in the data of Marti *et al* it rises from 0.988 at 573 K through 0.995 at 1353 K to 1.000 (metrically cubic) at 1673 K. We believe the data of Marti *et al* show anomalies related to the use of two different furnaces in their work.

There is, in space group $R\bar{3}c$, only one variable position parameter, the x -parameter of the O atom. We find that this decreases slowly, from 0.5565(2) at 383 K, through 0.5497(3) at 1373 K, to 0.547(1) at 1673 K. We shall discuss this further in the next section. To compare with the results from Marti *et al*, we find an equivalent position in their space group near our x , $0, \frac{1}{4}$, then read off their x -coordinate as 0.5601 at 573 K, 0.5527 at 1353 K, and 0.4826 at 1673 K. The rapid variation at the highest temperature, to a value less than 0.5, is an unexpected

and perhaps doubtful result.

4. Discussion

The main interest in our study was the rhombohedral phase of LaGaO_3 and the manner in which the rhombohedral structure changed with temperature. In rhombohedral space group $R\bar{3}c$, the only structural parameters are the oxygen position parameter x , and the (hexagonal) lattice parameters a and c . These determine a rotation angle and strain for the oxygen octahedron.

In this work, we have given the oxygen position as $x, 0, \frac{1}{4}$ with $x = \frac{1}{2} + u$, and $u = 0$ in the cubic perovskite. The oxygen at the equivalent position, $1/6 - u, 1/3, 1/12$, forms part of the oxygen octahedron around the Ga at the origin [16]. On the basis of these coordinates, it can be determined that the angle of rotation ϕ of the octahedron (away from its orientation in the cubic perovskite) is given by

$$\tan \phi = 2u\sqrt{3}. \quad (1)$$

Figure 3 shows how the octahedral rotation angle obtained from this relationship varies with temperature—it is about 11° at 383 K, reducing to 9.3° at 1673 K.

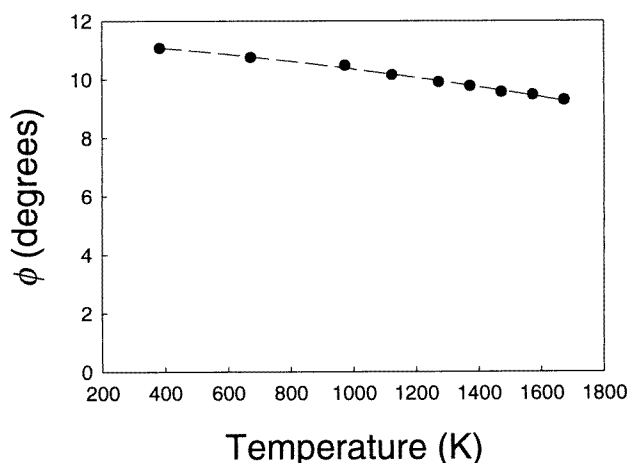


Figure 3. The temperature variation of the angle of rotation of the oxygen octahedron about the threefold axis of the rhombohedral phase. This angle would be zero in cubic perovskite.

The cubic structure in the hexagonal setting would have [2] $c/a = \sqrt{6}$, and were the octahedra in the rhombohedral structure tilted through angle ϕ but otherwise perfectly regular, we would have [15–17] $c/a = \sqrt{6}/\cos \phi$. In general we find

$$c/a = \eta\sqrt{6}/\cos \phi \quad (2)$$

in which η is the ‘octahedral strain parameter’, and $\eta > 1$, $\eta = 1$, $\eta < 1$ according as the octahedron is elongated in the direction parallel to the threefold axis (c -axis), regular, or compressed along this axis, respectively [15, 16]. We have used equations (1) and (2) to evaluate η from u , c , and a , and have examined its temperature variation (figure 4). We find that $\eta < 1$ (octahedra compressed along the threefold axis), but it increases quite linearly over the temperature range of this study. The octahedra become more regular as the temperature is increased.

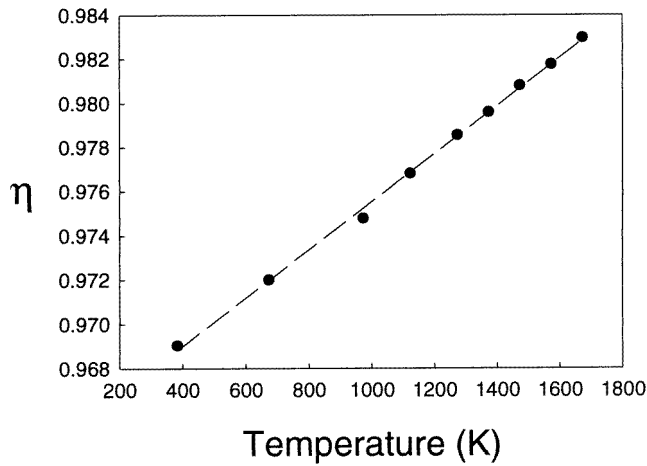


Figure 4. The temperature variation of the octahedral strain parameter in the rhombohedral phase. This would take the value one in cubic perovskite.

The octahedral rotation and the octahedral strain are, in the rhombohedral structure, two geometrically independent parameters. The question of whether there may be some physical coupling between the two parameters is, however, an interesting one. From a survey of the then published results on perovskites in $R\bar{3}c$, Megaw and Darlington [16] suggested a dependence of the strain on the square of the rotation angle:

$$1 - \eta \propto \phi^2. \quad (3)$$

Our present data on LaGaO_3 lie well to the right of the curve shown by Megaw and Darlington (their figure 5), and even considered apart from previous data (our figure 5) they cannot be fitted with a function of the form (3). Linear extrapolation might suggest that (were the compound stable) the octahedral strain would fall to zero with the rotation angle still at 7° . However, we

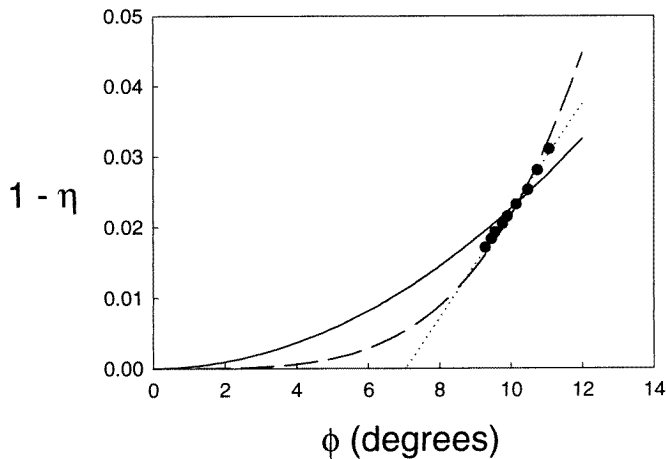


Figure 5. The correlation between octahedral strain and rotation angle in the octahedral phase. The continuous and broken curves represent best fits of the forms $\eta \propto \phi^2$ and $\eta \propto \phi^4$ respectively—the former is certainly not satisfactory. The dotted line shows a straight-line fit (see the text).

cannot rule out a coupling between rotation and octahedral strain involving a dependence of strain on some higher power (e.g. the fourth) of the angle of rotation.

Finally, it may of some interest to speculate, from the trends in octahedral strain and rotation, what might happen were the sample stable to higher temperatures. If the strain were coupled to the rotation, then it is likely that the octahedron would become regular as the rotation approached zero and the structure would become cubic at some higher temperature. If however the two were uncoupled, then it seems the octahedra would become regular while still rotated from their position in the ideal cubic structure. It can be seen from (2) that the structure could be rhombohedral but metrically cubic under the condition $\eta = \cos \phi$ —a condition which might (hypothetically) have occurred at around 2300 K, with $\phi \sim 8^\circ$, and $\eta = \cos \phi \sim 0.99$. In this context, it will be of interest to conduct similar detailed studies on rhombohedral $R\bar{3}c$ perovskites, which undergo transitions to the cubic phase.

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References

- [1] Kennedy B J and Hunter B A 1998 *Phys. Rev. B* **58** 653
- [2] Howard C J and Stokes H T 1998 *Acta Crystallogr. B* **54** 782
- [3] Kennedy B J, Howard C J and Chakoumakos B C 1999 *Phys. Rev. B* **59** 4023
- [4] Kennedy B J, Howard C J and Chakoumakos B C 1999 *J. Phys.: Condens. Matter* **11** 1479
- [5] Kennedy B J, Howard C J and Chakoumakos B C 1999 *Phys. Rev.* at press
- [6] Geller S 1957 *Acta Crystallogr.* **10** 243
- [7] Marti W, Fischer P, Altorfer F, Scheel H J and Tadin M 1994 *J. Phys.: Condens. Matter* **6** 127
- [8] O'Bryan H M, Gallagher P K, Berkstresser G W and Brandle C D 1990 *J. Mater. Res.* **5** 183
- [9] Sandstrom R L, Giess E A, Gallagher W J, Segmüller A, Cooper E I, Chisholm M F, Gupta A, Shinde S and Laibowitz R B 1988 *Appl. Phys. Lett.* **53** 1874
- [10] Miyazawa S 1989 *Appl. Phys. Lett.* **55** 2230
- [11] Glazer A M 1972 *Acta Crystallogr. B* **28** 3384
- [12] Chakoumakos B C 1997 *Physica B* **241–243** 361
- [13] Hill R J and Howard C J 1986 *Australian Atomic Energy Commission (now ANSTO) Report M112*
- [14] Caglioti G, Paoletti A and Ricci F P 1958 *Nucl. Instrum.* **3** 223
- [15] Thomas N W 1996 *Acta Crystallogr. B* **52** 954
- [16] Megaw H D and Darlington C N W 1975 *Acta Crystallogr. A* **31** 161
- [17] Megaw H D 1973 *Crystal Structures: a Working Approach* (Philadelphia, PA: Saunders) ch 12, p 296