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Bond-Valence Analysis of the Structure of $(Ba_{0.875}Sr_{0.125})RuO_3$

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The structure of $TRuO_3$($T = Ba_{0.875}Sr_{0.125}$) has been analyzed using the bond valence procedures developed by Brown [e.g., *Acta Crystallogr. Sect. B* 48, 553 (1992)] and O'Keeffe [*Structure and Bonding* 71, 161 (1989)]. The experimental results, which show "overbonded" and "underbonded" *T* and Ru cations, respectively, are explained by the fact that the theoretical *T*–O and Ru–O distances that completely satisfy the valence requirements of the atoms are incommensurate under the constraints imposed by the site symmetries of the special positions occupied by the atoms. Starting from a model derived from sphere packing geometry and the theoretical bond lengths, it is possible to evaluate the lattice parameters and the atomic shifts that minimize the strains introduced into the structure by the incommensurability of the theoretical Ru–O and *T*–O distances, and to arrive at a model quite close to the experimental results without making use of any prior knowledge of the structure. According to this analysis, therefore, the observed structure is interpreted as resulting from a compromise between the different bond distance requirements of the Ru and *T* cations.

Key Words: **structural modeling; bond-valence method; sphere packing; barium strontium ruthenium oxide.**

INTRODUCTION

One way to gain insight into the crystal chemistry of a large number of oxide compounds is to model their structures in terms of bond valences and their corresponding bond distances. The general principles of the bond valence method have been fully developed (1–4) and may be summarized by writing the equations

$$v_{ij} = \exp[(R_{ij} - d_{ij})/0.37] \quad \text{and} \quad d_{ij} = R_{ij} - 0.37 \ln v_{ij} \qquad [1]$$

$$\sum_j v_{ij} = V_i \qquad [2]$$

$$\sum_{\text{loop}} v_{ij} = 0, \qquad [3]$$

where v_{ij} is the bond valence associated with a bond of length d_{ij} between atoms i and j, the bond valence parameter R_{ij} is the distance corresponding to a bond valence $v_{ij} = 1.0$ v.u., and V_i is the valence of atom i. The parameters R_{ij} depend on the nature and the valences of atoms i and j, and their values have been tabulated for most atomic species (5–7). A significant advantage of the bond valence method of interpretation is that it makes no *a priori* assumption as to the nature of the chemical bond.

In many cases, a comparison between the theoretical atomic valences and the bond valence sums calculated from the observed bond distances allows us: (i) to check the correctness of a structure determination; (ii) to locate atoms that are difficult to identify by X-ray or neutron diffraction (such as O and F, for example); (iii) to distinguish between oxidation states of transition metals. When the observed bond lengths are affected by factors other than the valences of the atoms involved in the bonding, however, the "apparent" bond valences v'_{ij} calculated from them do not satisfy Eqs. [2] and [3] and, as a consequence, the above procedure cannot be used to analyze the experimental structures. In these cases, bond valences are calculated first from a system of Eqs. [2] and [3], and from these the corresponding bond lengths are obtained. These are the distances that satisfy exactly the valence requirements of the atoms; i.e., they are the distances that would exist in a structure without crystallographic constraints. This ideal configuration must be changed to conform to an assumed or known space group symmetry and other steric requirements imposed by the initial model of the structure. From this point, a modeling process is carried out in which lattice and positional parameters are varied until the extent to which Eqs. [2] and [3] are violated over the whole structure is minimized. Remarkable examples of the application of this method are provided by a study of the strain relaxation mechanisms in $YBa_2Cu_3O_x$, for $x = 6.0$ and 7.0 (8), and by the prediction of the crystal structures and phase diagram in the system La_2NiO_{4+x} (3).

Since initial models can be easily derived from any assumed packing sequence, structures based on sphere packing geometry provide ideal systems to test the power of the

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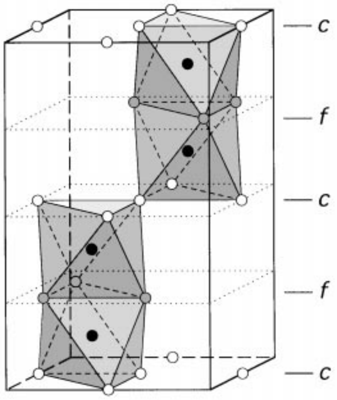

FIG. 1. Schematic representation of the structure of $T\mathrm{RuO}_3$ ($T = \mathrm{Ba}_{0.875}\mathrm{Sr}_{0.125}$), showing the $\mathrm{Ru}_2\mathrm{O}_9$ dimers of the face-sharing RuO_6 octahedra. The dimers are joined together by corner-sharing. The letters c and f indicate the layers on which the octahedra share corners and faces, respectively.

bond valence method for predicting crystal structures. In an ongoing research program on Ru-based oxides, a number of compounds were prepared (9), with structures that are based on close packing of hexagonal $A\mathrm{O}_3$ layers stacked on top of one another with a variety of sequences. Bond valence sums calculated from the observed bond distances invariably show significant departures from the expected atomic valences. Based on the quality of the agreement between observed and calculated intensities (10), these discrepancies cannot be attributed to errors in the structural models, and a possible explanation of the observed anomalies could be the presence of internal strains. In view of this, we decided to apply the bond-valence method to the relatively simple case of a four-layer compound, $T\mathrm{RuO}_3$ ($T = \mathrm{Ba}_{0.875}\mathrm{Sr}_{0.125}$) (Fig. 1), with the purpose not only of predicting its structure, and thus confirming or excluding the presence of internal strains, but also of gaining insight into the geometrical factors that affect the final configuration of the atoms.

MODELING OF THE STRUCTURE

A. …cfcf… Packing of Spheres

If we assume a structure $AB\mathrm{O}_3$ in which the A and O spheres are packed to form hexagonal $A\mathrm{O}_3$ layers, and if we stack these layers on top of each other so that the $B\mathrm{O}_6$ octahedra share faces and corners alternately along the direction of stacking, we obtain a configuration that may be represented with the sequence

$$\left[\begin{array}{ccccccccc} c & & f & & c & & f & & \\ 0,0,0 & & \frac{2}{3},\frac{1}{3},\frac{1}{4} & & 0,0,\frac{1}{2} & & \frac{1}{3},\frac{2}{3},\frac{3}{4} & & \\ X & & Y & & X & & Z & & \\ & B(1) & & B(2) & & B(3) & & B(4) & \\ & \frac{1}{3},\frac{2}{3},\frac{1}{8} & & \frac{1}{3},\frac{2}{3},\frac{3}{8} & & \frac{2}{3},\frac{1}{3},\frac{5}{8} & & \frac{2}{3},\frac{1}{3},\frac{7}{8} & \end{array}\right].$$

TABLE 1

Structural Model Derived from the Sequence…*XYXZ*… for a Compound TBO$_3$ (Space Group $P6_3/mmc$ $a = 5.8$ Å, $c = 9.5$ Å)

Atom	Position	x	y	z
$T(1)$	$2a\ \bar{3}m$	0	0	0
$T(2)$	$2c\ \bar{6}m2$	1/3	2/3	1/4
Ru	$4f3m$	2/3	1/3	$z_\mathrm{R} = 1/8$
O(1)	$6g\ 2/m$	1/2	1/2	0
O(2)	$6h\ mm$	$2x_0$	$x_0 = 1/6$	1/4

In this scheme, the symbols X, Y, Z represent the $A\mathrm{O}_3$ layers; the triplets on top of each layer represent the coordinates of A referred to the natural hexagonal axes; and the letters c and f specify whether the layer is one on which the $B\mathrm{O}_6$ octahedra share corners or faces, respectively. The B atoms are located between the $A\mathrm{O}_3$ layers with the coordinates indicated at the bottom of the sequence. The coordinates show that atoms $B(1)$ and $B(2)$ (and atoms $B(3)$ and $B(4)$) are directly superposed at a distance $c/4$, where c is the direction of stacking, while cations $B(2)$ and $B(3)$ are shifted from one another by $\frac{1}{3},\frac{2}{3},\frac{1}{4}$. As a consequence of this configuration, the $B(1)\mathrm{O}_6$ and $B(2)\mathrm{O}_6$ octahedra share a face (as $B(3)\mathrm{O}_6$ and $B(4)\mathrm{O}_6$ do), while $B(2)\mathrm{O}_6$ and $B(3)\mathrm{O}_6$ share corners. The structure corresponding to this configuration has the symmetry of space group $P6_3/mmc$, with the atomic coordinates indicated in Table 1. If the A and O spheres have the same radius r, the lattice parameters of the structure are $a_\mathrm{H} = 4r$, $c_\mathrm{H} = 8r\sqrt{\frac{2}{3}}$, i.e., $c_\mathrm{H}/a_\mathrm{H} = 2\sqrt{\frac{2}{3}}$. If we assume the radii $\mathrm{Ba}^{2+}(\mathrm{XII}) = 1.61$ Å, $\mathrm{Sr}^{2+}(\mathrm{XII}) = 1.44$ Å, and $\mathrm{O}^{2-}(\mathrm{VI}) = 1.40$ Å (11) the average value of r is 1.45 Å, and therefore $a_\mathrm{H} = 5.8$ Å and $c_\mathrm{H} = 9.5$ Å.

B. Determination of Bond Valences

The interpretation of Eqs. [2] and [3] and the procedures used to set up a system of equations sufficient to determine uniquely the unknowns v_{ij}, are described in detail in a number of papers (e.g., (3, 4)). The case of our model is illustrated in Table 2, where the formula unit, the atomic coordinations, the connectivity matrix (4), the system of Eqs. [2] and [3], and the calculated values of v_{ij} have been indicated. With our conditions, the bond valences of all the T–O bonds are equal to $\frac{1}{6}$ v.u., and those of the two Ru–O bonds are $\frac{2}{3}$ v.u. From these v_{ij} we may calculate the corresponding bond distances d_{ij} using the values of the bond valence parameters R_{ij} (Å): Ba–O = 2.29, Sr–O = 2.118, T–O = 2.269, Ru^{4+}–O = 1.834. The results of the calculations described so far are given in column 1 of Table 3. We want to point out that the bond distances T–O = 2.932 Å and Ru–O = 1.984 Å are the theoretical separations that

TABLE 2
Formula Unit, Atomic Coordinations, Connectivity Matrix and Bond-Valence Sum Equations for the Structure of $\mathbf{TRuO_3}$

Formula unit: $T(1)T(2)B_2\mathrm{O}(1)_3\mathrm{O}(2)_3$

Atomic coordinations:

$\{T(1)\}\mathrm{O}(1)_6\mathrm{O}(2)_6$ $\{T(2)\}\mathrm{O}(1)_6\mathrm{O}(2)_6$

$\{B\}\mathrm{O}(1)_3\mathrm{O}(2)_3$

$\{\mathrm{O}(1)\}T(1)_2T(2)_2B_2$ $\{O(2)\}T(1)_2T(2)_2B_2$

$$\left\{\begin{array}{ccc} & 3\mathrm{O}(1) & 3\mathrm{O}(2)\\ T(1) & 6\times v_{11} & 6\times v_{12}\\ T(2) & 6\times v_{21} & 6\times v_{22}\\ 2B & 6\times v_{31} & 6\times v_{32}\end{array}\right\}$$

with $T = \mathrm{Ba}_{0.875}\mathrm{Sr}_{0.125}$
and $B = \mathrm{Ru}$:[a]

$$\begin{cases} 3v_{11} + 3v_{12} = 1\\ 3v_{21} + 3v_{22} = 1\\ 3v_{31} + 3v_{32} = 4\\ v_{11} + v_{21} + v_{31} = 1\\ v_{11} - v_{12} + v_{22} - v_{21} = 0\\ v_{11} - v_{12} + v_{32} - v_{31} = 0\end{cases}$$

$v_{11} = v_{12} = v_{21} = v_{22} = 1/6$
$v_{31} = v_{32} = 2/3$

[a] Since

$$\frac{v_{1i}}{v_{2i}} = 1 = \frac{V_{T(1)}}{V_{T(2)}} \quad \text{and} \quad \frac{V_{i1}}{V_{i2}} = 1 = \frac{3V_{\mathrm{O}(1)}}{3V_{\mathrm{O}(2)}}$$

this matrix can be solved with the method of O'Keeffe given in Ref. (4).

TABLE 3
Models of the Structure of $\boldsymbol{T}\mathbf{RuO_3}$

	1	2	3	4	5	6
a		5.864	5.750	5.750	5.7179(1)	0.032
c		9.576	9.390	9.390	9.4897(2)	– 0.100
c/a		1.633	1.633	1.633	1.6596(1)	– 0.027
x_0	1/6	1/6	1/6	0.1770	0.1769(2)	0.000
z_{R}	1/8	1/8	1/8	0.1175	0.1167(2)	0.001
			Bond valences			
$T(1)$–O(1) × 6	0.167	0.167	0.194	0.194	0.203	– 0.009
$T(1)$–O(2) × 6	0.167	0.167	0.194	0.165	0.159	0.006
$T(2)$–O(1) × 6	0.167	0.167	0.194	0.165	0.159	0.007
$T(2)$–O(2) × 6	0.167	0.167	0.194	0.193	0.202	– 0.009
Ru–O(1) × 3	0.667	0.524	0.584	0.651	0.660	– 0.009
Ru–O(1) × 3	0.667	0.524	0.584	0.651	0.640	0.011
			Bond-valence sums			
$T(1)$	2.00	2.00	2.33	2.16	2.17	
$T(2)$	2.00	2.00	2.33	2.33	2.33	
Ru	4.00	3.14	3.50	3.90	3.90	
O(1)	2.00	1.72	1.95	2.08	2.10	
O(2)	2.00	1.72	1.95	2.02	2.00	
R	0.00	0.42	0.31	0.17	0.18	
			Bond distances			
$T(1)$–O(1)	2.932	2.932	2.875	2.875	2.8589(1)	0.016
$T(1)$–O(2)	2.932	2.932	2.875	2.936	2.950(1)	– 0.014
$T(2)$–O(1)	2.932	2.932	2.875	2.875	2.8901(1)	– 0.015
$T(2)$–O(2)	2.932	2.932	2.875	2.877	2.8607(1)	0.016
Ru–O(1)	1.984	2.073	2.033	1.993	1.988(1)	0.005
Ru–O(2)	1.984	2.073	2.033	1.993	2.000(2)	– 0.007
Ru–Ru		2.394	2.347	2.488	2.528(3)	– 0.040
O(2)–O(2)		2.932	2.875	2.697	2.683(3)	0.014

Note. 1, data obtained from the bond valence sum equations; 2, commensurate structure assuming $a = 2[T\text{–O}] = 5.864$ Å; 3, model obtained with the lattice parameters that minimize the R index (Fig. 2); 4, model obtained by changing x_0 and z_{R} according to Eqs. [5] and [6]; 5, experimental structure (10); 6, differences 4 – 5.

satisfy the valence requirements of the atoms, and they are not necessarily commensurate to form a structure constrained as indicated in Table 1. In order to find out whether this is the case for our model, we need to make use of the bond distance equations shown in Table 4. From these expressions it can be seen that the equality of all the T–O and Ru–O separations can be preserved if, and only if, $x_0 = \frac{1}{6}$, $z_R = \frac{1}{8}$, and $c = 2a\sqrt{\frac{2}{3}}$. With these parameters and with $a = 2[T(1)\text{–O}(1)] = 5.864$ Å, we obtain the structure of column 2 of Table 3. The value Ru–O = 2.073 Å evaluated for this model is much larger than the theoretical distance of 1.984 Å predicted by the bond valence sum equations and indicates that the theoretical T–O and Ru–O distances that satisfy Eqs. [2] and [3] are incommensurate under the geometrical constraints imposed by space group symmetry and special position assignments of our model. Under these conditions, structural strains are unavoidable and we should therefore expect contractions and expansions of the T and Ru coordination polyhedra. In the structure of column 2, the valences $V(\mathrm{Ru}) = 3.14$ v.u. and $V(\mathrm{O}) = 1.72$ v.u. are far too low compared with the expected values of 4.0 and 2.0 v.u., respectively. An equivalent result, but with the polyhedra around the T atoms considerably contracted, is obtained if we calculate the a parameter with the expression $a = 2[\mathrm{Ru\text{–}O}]\sqrt{2} = 5.612$ Å. With this assignment we obtain, from Table 4, $c = 9.164$ Å, T–O = 2.806 Å, and $V(T) = 2.81$ v.u. (We want to point out that the experimental lattice parameters, $a = 5.718$ Å and $c = 9.490$ Å, are between these values and those reported in column 2.)

The discrepancies between calculated and expected valences are reflected by the high value of the index R (0.42 v.u.), which is the root mean square of the differences between the valence sums around each atom and the corresponding theoretical valences, i.e.,

$$R = \left[\frac{\sum_i(\sum_j v'_{ij} - V_i)^2}{n}\right]^{1/2} \quad 1 \le i \le n. \qquad [4]$$

TABLE 4
Bond Distance Equations for the Structure of TRuO$_3$

$T(1)$–O(1)	$= a/2$
$T(1)$–O(2)	$= (3x_0^2a^2 + c^2/16)^{1/2}$
$T(2)$–O(1)	$= (a^2/12 + c^2/16)^{1/2}$
$T(2)$–O(2)	$= (\frac{1}{3} + 3x_0^2 - x_0)^{1/2}a$
Ru–O(1)	$= (a^2/12 + z_R^2c^2)^{1/2}$
Ru–O(2)	$= [(3x_0^2 - 2x_0 + 1/3)a^2 + (z_R^2 - z_R/2 + \frac{1}{16})c^2]^{1/2}$
O(2)–O(2)	$= (1 - 3x_0)a$
Ru–Ru	$= (1/2 - 2z_R)c$

In this expression, v'_{ij} are the "apparent" bond valences that are obtained by forcing the bond distances to be commensurate. From this definition it follows that R is a measure of the extent to which Eq. [2] is violated over the whole structure (3). A value of R larger than about 0.2 v.u. is an indication that the structure may not be stable at room temperature, and consequently the model of column 2 is unacceptable.

C. Relaxation of the Structure

The most obvious mechanism to relax the model of column 2 is to reduce the Ru–O distance by decreasing the a and c lattice parameters. The procedure used in the present case has been to decrease a and c in steps by keeping (i) the c/a ratio fixed at $2\sqrt{\frac{2}{3}}$, and (ii) the z_R and x_0 positional parameters fixed at their aristotype values of $\frac{1}{8}$ and $\frac{1}{6}$, respectively. Under these conditions, the equality of the bond distances, required by the bond valence sum equations, is preserved. For each value of a, bond distances were calculated, and from these were calculated the bond valences, bond valence sums, and the index R. The plot of R versus a, shown in Fig. 2, has a minimum corresponding to $a \cong 5.75$ Å, $c = 9.39$ Å. The model obtained with these lattice parameters is shown in column 3 of Table 3. The effect of reducing the unit cell volume has been to decrease both T–O and Ru–O distances, and thus increase the apparent valences of both T and Ru. As a consequence of these changes, the new index R of 0.31 v.u. is much better than the previous one, but still too high to ensure a stable structure.

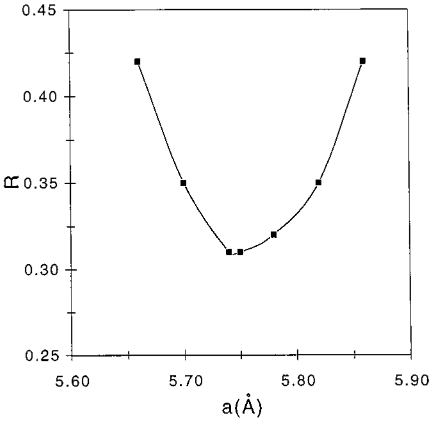

FIG. 2. Plot of the R index versus the lattice parameter a.

A second step for relaxing the model consists in varying the positional parameters z_R and x_0 so that $V(\text{Ru})$ increases and $V(T)$ decreases. The bond valence equations show that the Ru–O(1) distance can be decreased only by decreasing the value of z_R. However, the expression $(z_R^2 - z_R/2 + \frac{1}{16})$, which appears in the equation of Ru–O(2), will increase when z_R decreases, because z_R^2 is much smaller than z_R (z_R is of the order of 0.1). In order to decrease also Ru–O(2), therefore, we have to increase x_0. An increase of x_0, however, will correspond to a decrease of the O(2)–O(2) distance. Assuming an O(2)–O(2) separation of 2.7 Å as a lower limit for an acceptable nonbonded distance, and imposing the condition Ru–O(1) = Ru–O(2), as required by the bond-valence sum equations, we have

$$x_0 = \frac{a - 2.7}{3a} \quad [5]$$

and

$$z_R = \left(6x_0^2 - 4x_0 + \frac{1}{2}\right)\frac{a^2}{c^2} + \frac{1}{8}. \quad [6]$$

DISCUSSION

The final model, obtained with the distance O(2)–O(2) = 2.7 Å, is reported in column 4 of Table 3 and is compared with the experimental results shown in column 5. Bond distances agree well within 0.02 Å, and bond valences better than 0.01 v.u. The close agreement between calculated and observed values provides strong evidence that the factors taken into consideration in modeling the structure are basically those that affect the arrangement of the atoms in the real structure. These factors can be summarized as follows: (i) the basic atomic configuration, including space group symmetry and Wyckoff positions of the atoms, is dictated by the geometry governing the close packing of spheres; (ii) the lattice parameters of the hexagonal cell are the result of a compromise to fit together the incommensurate Ru–O and T–O distances demanded by the Ru and T valence requirements; and (iii) the shifts of z_R and x_0 from their aristotype values have the effect of pulling apart the two Ru atoms inside the face-sharing RuO$_6$ octahedra and of interposing oxygen atoms O(2) between these atoms, as shown in Fig. 3. This last factor is the so-called "shielding effect," resulting in a configuration in which the Ru–O(2) distances are shortened and the valence requirements of Ru and O are

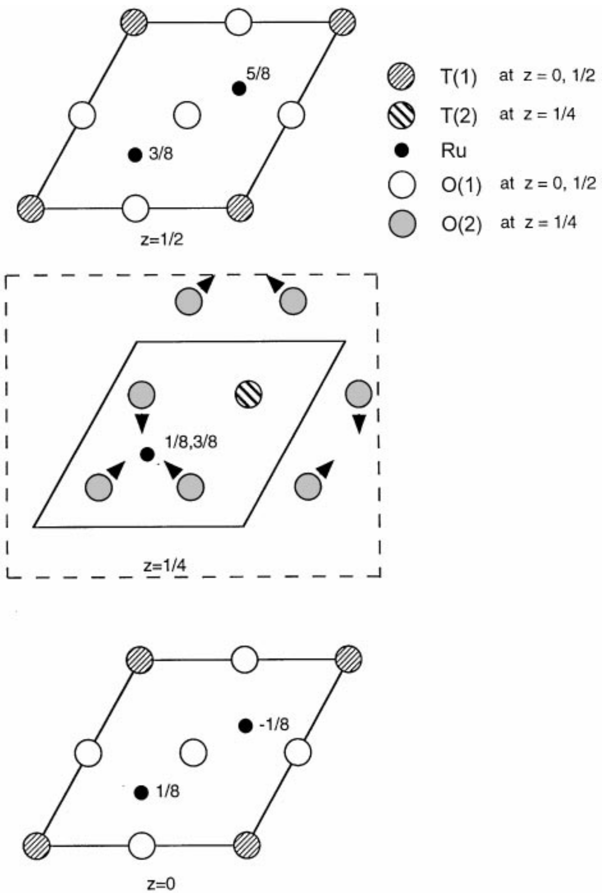

FIG. 3. The arrows represent the shifts caused by an increase of the atomic coordinate x_0, defined in Table 1. The z coordinates of Ru atoms are indicated next to the small full circles representing these atoms in the figure.

satisfied better than by placing the atoms in their aristotype positions. The bond-valence sum of Ru gives $V(\mathrm{Ru}) = 3.90$ v.u. This value is close to the expected valence of Ru in this compound (4.00 v.u.), and it indicates that Ru interacts predominantly with oxygen. Direct Ru–Ru interactions, if present, must therefore be weak. This conclusion is consistent with electric measurements showing that the compound is a semiconductor at room temperature (9).

The worst agreement between observed and calculated values is obtained for the c parameter and the Ru–Ru distance. These discrepancies may well be due to the same cause. The Ru–Ru separations determined experimentally in compounds similar to $T\mathrm{RuO_3}$ are larger than the distance of 2.49 Å of our model. For example, separations of about 2.7 Å were found in compounds of formula $Ba_3MRu_2O_9$ ($M = $ Zn, Co, Ni), which have the same Ru_2O_9 units of face-sharing octahedra (12, 13). A value of 2.53 Å was found for the nine-layer structure of $BaRuO_3$ (10). The only mechanism left to increase the Ru–Ru distance in our model would be to increase the c parameter. This change would also improve the values of $V(T1)$ and $V(T2)$. This gain, however, would be offset by the fact that the Ru–O distance would also increase, lowering $V(\mathrm{Ru})$ below 3.9 v.u. At this stage, the method is probably not sensitive enough to permit a further refinement of the model, and for this reason no attempts were made to change the c parameter from its final value of 9.39 Å.

Strained structures are formed when it is geometrically impossible to accommodate the bond distances calculated from the atomic valences in a configuration defined by a given set of constraints. Our analysis proves that, within these constraints, a strained structure will always tend to assume a configuration that optimizes the bond-valence sums of the atoms. In the case of $T\mathrm{RuO_3}$, for example, the lattice parameters could be adjusted to values close to the experimental results by simply minimizing the R index. Other steric factors, however, also play a role and have to be monitored in building a model. Thus, the shifts of the z_{R} and x_0 positional parameters were limited by the shortening of the O(2)–O(2) separations below acceptable values. Finally, we want to point out that the building of our model has been carried out without taking into consideration any of the experimental results. This is the same as saying that the structure of column 4 in Table 3 has been determined *ab initio*, ignoring any prior knowledge of the structure. Similar analyses designed to explore the general applicability of this approach and based on different sphere packing schemes are now being made or are under consideration, and the results will be published in due course.

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