BOND VALENCE ANALYSIS OF RUTHENATES

Bond valence analysis allows us to evaluate, for any compound whose bonding scheme is known or assumed, the bond distances that the atoms would form in an ideal structure in which all atomic valences are exactly balanced. In a significant number of cases this information is sufficient to make accurate predictions about the real crystal structure of the compound.

The bond valence method is based on two concepts that can be stated in the following way.

(i) A bond valence $v_{ij} = v_{ji}$ is assigned to a bond between atoms i and j, of valences $V(i)$ and $V(j)$, so that

$$\sum_{1}^{n(i)} {}_{j} v_{ij} = V(i) \quad \text{and} \quad \sum_{1}^{n(j)} {}_{i} v_{ji} = V(j) \qquad (1)$$

where $n(i)$ and $n(j)$ are the number of atoms in the coordination spheres of i and j, respectively. This principle of local valence balance is a generalization of Pauling's principle of local charge balance in ionic crystals, and is known as the *valence sum rule* [1].

(ii) The sum of the bond valences around any loop in the structure, taken with alternating signs, is equal to zero

$$\sum_{loop} v_{ij} = 0. \qquad (2)$$

Equation (2) expresses the mathematical conditions that result in the most regular distribution of the valences among the bonds in a structure and is known as the *equal valence rule* [1]. The system of equations (1) and (2) allows us to evaluate the valences of all the individual bonds if we know how the atoms are bonded together in a structure [2]. The description of atomic bonding in terms of bond valences is useful because the length d_{ij} of a bond between atoms i and j is a function only of the bond valence v_{ij}. The relationship between these two quantities is expressed by the empirical formula

$$d_{ij} = R_{ij} - 0.37 \ln v_{ij} \qquad (3)$$

where the bond valence parameter R_{ij} depends on the nature and the oxidation states of atoms i and j forming the bond, and expresses the length of a bond of unit valence. Values of R_{ij} can be evaluated from the bond distances of known structures and are tabulated for most chemical species [3,4]. By means of equations (1-3) we may evaluate the expected bond lengths for any known atomic configura-
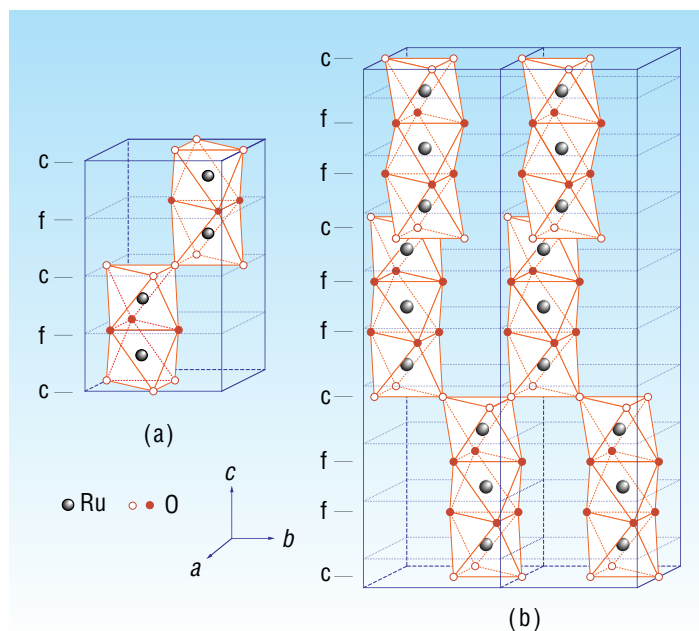

FIGURE 1. Schematic representation of (a) the 4-layer structure of $TRuO_3$ (T = 0.875 Ba + 0.125 Sr); and (b) the 9-layer structure of $BaRuO_3$. For clarity only the Ru and O atoms are shown in the figure. The symbols c and f indicate the layers on which the RuO_6 octahedra share corners and faces, respectively.

tion. These distances satisfy exactly the valence requirements of the atoms and, in general, differ significantly from those determined experimentally. The discrepancies are in some cases due to the electronic behavior of particular cations, which may cause distortions not accounted for by the bond valence model (for example, lone pair distortions around cations such as Bi^{3+} and Pb^{2+}, or Jahn-Teller distortions around Mn^{3+} and Cu^{2+}). In the majority of cases, however, the bond lengths calculated with equations (1-3) are incommensurate under the constraints imposed by the crystal geometry, and have to be stretched or compressed in order to fit them into a particular configuration. Since these changes introduce strains into the structure, the process of adapting the theoretical model to the requirements of a space group symmetry must be carried out in such a way that the violations of the bond valence sum rule and of the equal valence rule are kept as small as possible. We have recently applied the concepts discussed above to the determination of the crystal structures of $TRuO_3$ (T = 0.875Ba + 0.125Sr) [5] and $BaRuO_3$ [6], using initially only the information obtained from the indexing of the neutron diffraction patterns of these materials (i.e., crystal system symmetry and lattice parameters), and ignoring any

A. Santoro
NIST Center for Neutron Research
National Institute of Standards and Technology
Gaithersburg, MD 20899-8562

I. Natali Sora
INFM and Department of Physics and Chemistry
University of Brescia
25123 Brescia, Italy

Q. Huang
Department of Physics
University of Maryland
College Park, MD 20742

other structural details obtained in the experimental work. Since T^{2+} and Ba^{2+} have ionic radii similar to that of O^{2-}, we may expect that the structures of $TRuO_3$ and $BaRuO_3$ are built with some sphere packing mechanism. This assumption is corroborated by the fact that in both cases the a-parameter calculated from the average r of the ionic radii of A and O ($A = T$, Ba) for the composition AO_3 is in good agreement with the experimental values, and by the fact that the ionic radius of Ru^{4+} is quite close to the radius of the octahedral void formed by the close packing of oxygen anions. The periodicity n of the stacking sequences of the AO_3 layers in the vertical direction of the c-axis, evaluated with the formula $n = c/(2r\sqrt{2/3})$, shows that $TRuO_3$ and $BaRuO_3$ have 4- and 9-layer structures, respectively, in which the RuO_6 octahedra are related to one another as indicated in Fig. 1a and 1b.

In order to fit this configuration, the theoretical bond lengths calculated with equations (1-3) have to be changed, and in particular the A-O bonds have to be compressed, on the average, and the

Ru-O bonds have to be stretched. This process of relaxation of the initial model is carried out by modifying the structural parameters obtained from sphere packing geometry in such way that the violations of equations (1) and (2) are contained within reasonable bounds [7]. The results of the bond valence analysis of $BaRuO_3$ are reported in Table 1, where they are compared with the corresponding values determined experimentally. Similar results, reported in reference [5], were obtained for $TRuO_3$. The agreement between the observed and calculated structures is quite good for both compounds, and the differences between bond distances are well within 0.02 Å. This result proves that, at least in favorable cases, the bond valence method may yield an accurate model of the structure without requiring more information than that needed to index a powder pattern. More importantly, however, it shows that the need to satisfy the valence requirements of the atoms with an acceptably regular distribution of the bond valences is the driving force in determining the magnitude and the direction of the atomic shifts allowed by the symmetry, and that, as a consequence, non-bonded metal-metal and oxygen–oxygen interactions do not play an important role in the way in which the structures of these ruthenates are built. In particular, the shifts that pull together the oxygen atoms forming the shared faces of the RuO_6 octahedra (thus providing a shielding effect to Ru-Ru interactions) are specifically designed to improve the local valence balance of the Ru and O atoms involved in the Ru-O bonds. Application of the method to structural types other than perovskites is now under consideration.

Table 1. Models of the Structure of $BaRuO_3$ (R $\bar{3}$ m)

	1	2	3	4
Lattice parameters (Å) and atomic positions				
a	5.754	5.754	5.747(1)	0.007
c	21.142	21.626	21.602(1)	0.024
x	1/6	0.1769	0.1769(1)	0.0000
z_1	1/9	0.1087	0.1082(1)	0.0005
z_2	2/9	0.2185	0.2175(1)	0.0010
z_3	7/18	0.3844	0.3829(1)	0.0015
Bond distances (Å)				
Ba(1)-O(1)	2.877	2.877	2.8733(1)	0.004
-O(2)	2.877	2.938	2.926(2)	0.012
Ba(2)-O(1)	2.877	2.988	3.002(2)	-0.014
-O(2)	2.877	2.882	2.880(2)	0.002
-O(2')	2.877	2.957	2.945(3)	0.012
Ru(1)-O(1)	2.034	2.001	2.005(2)	-0.004
Ru(2)-O(1)	2.034	1.995	1.974(1)	0.021
-O(2)	2.034	1.995	2.007(2)	-0.012

Note. 1, commensurate structure derived from sphere packing geometry; 2, model obtained with the relaxation process discussed in the text; 3, experimental results; 4, difference between calculated and observed values. The theoretical bond distances calculated with equations (1-3) are: T-O = 2.932 Å, Ba-O = 2.948 Å and Ru-O = 1.984 Å.

REFERENCES

[1] D. Brown, Acta Cryst. B**48**, 553 (1992).

[2] M. O'Keeffe, Structure and Bonding **71**, 161 (1989).

[3] D. Altermatt and I. D. Brown, Acta Cryst. B**41**, 240 (1985); I. D. Brown and D. Altermatt, Acta Cryst. B**41**, 244 (1985).

[4] N. E. Breese and M. O'Keeffe, Acta Cryst. B**47**, 192 (1991).

[5] A. Santoro, I. Natali Sora and Q. Huang, J. Solid State Chem. **143**, 69 (1999).

[6] A. Santoro, I. Natali Sora and Q. Huang, (in preparation).

[7] I. D. Brown, Z. Kristall. **199**, 255 (1992).