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On the Distortion of the NiO_6 Octahedron in $BaNiGd_2O_5$

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The NiO_6 octahedron in $BaNiGd_2O_5$ is tetragonally distorted with two short and four long bonds, and has a further 10° orthorhombic distortion of the angles in the equatorial plane. These distortions are shown to arise from the strain required to maintain commensurability between the Ni–O and Gd–O bonds along the **a** axis. The high strain energy in the structure is reduced by the relaxation of the *d*-electrons of the Ni atoms as shown by Burdett and Mitchell (*J. Am. Chem. Soc.* **112,** 6571 (1990)).

1. Introduction

Using crystal field theory, Burdett and Mitchell (*1*) have shown that the distortion found in the octahedral environment of the Ni atom in $BaNiGd_2O_5$ is stabilized by the relaxation of the *d* electrons. The structure, refined by Amador *et al.* (*2*) (Fig. 1 and Table I, Col. 2), contains chains of corner-linked NiO_6 octahedra running along the **a** axis. The environment of the Ni atom shows two distortions, a tetragonal distortion in which the two bridging Ni–O(2) bonds are shortened to 1.89 Å while the four terminal Ni–O(1) bonds are lengthened to 2.20 Å, and an orthorhombic distortion in which pairs of equatorial O(1) atoms move closer together to give O(1)–Ni–O(1) angles of 80° and 100°.

Burdett and Mitchell invoke the interaction between the d_{z^2} orbitals on the two Ni atoms bonded to O(2) to explain the tetragonal distortion (*3*). This interaction breaks the degeneracy of the octahedral *Eg* levels by raising the energy of the d_{z^2} orbital. Instead of the two electrons having parallel spins as is normal in oxides, both are spin-paired in the lower energy $d_{x^2-y^2}$ orbital. Since these are antibonding orbitals, the Ni–O(2) bond is strengthened (and hence shortened) and the Ni–O(1) bond is weakened. The bonding is further stabilized by the equatorial O atoms moving away from the directions of the occupied antibonding $d_{x^2-y^2}$ orbitals, thus favoring the orthorhombic distortion, which Burdett and Mitchell suggest is caused by crystal packing.

The purpose of this paper is to show that both observed distortions can also be predicted from crystal packing considerations alone without invoking any electronic effects. The structure is modeled in three steps. The first is to construct a finite bond diagram directly from the chemical formula, the second is to expand this diagram into an infinite structure in Euclidean space, and the third is to adjust the atomic positions to provide optimum bonding. The procedure is described in Section 2 and the structure is modeled in Section 3. The results, discussed in Section 4, show that the electronic rearrangement described by Burdett and Mitchell is a response to the strain in the crystal and stabilizes what would otherwise be a sterically unstable structure.

2. Procedure for Modeling the Structure

The first step in modeling the structure is to develop a chemical bond diagram (Fig. 2) from the chemical formula. In

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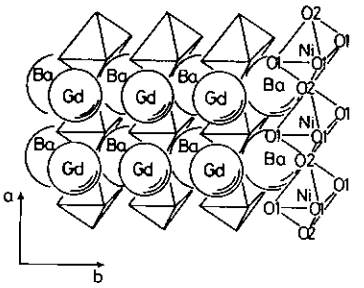

FIG. 1. The structure of $BaNiGd_2O_5$. The chains of NiO_6 are shown as linked octahedra extending along the **a** axis. Small circles are Gd and large circles Ba. The three-dimensional structure is generated by translating the layer shown by $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ so that the Gd atoms of one layer lie between the two O(1) atoms from different octahedra in the adjacent layer.

Section 3 it is shown that for $BaNiGd_2O_5$ this can be done without a prior knowledge of the crystal structure. In a chemical bond diagram, each bond is represented by a single line drawn between two atoms. Such a bond diagram may look unfamiliar but it is the inorganic equivalent of the well-known two-dimensional molecular diagram of organic chemistry, from which it differs only in that the infinitely connected network of bonds is folded back into a finite graph, giving, in some cases, more than one bond between the same pair of atoms. A double line in the bond diagram indicates two separate bonds, not a bond of order 2. Bond orders (bond valences) are not shown on the diagram and, in any case, are usually nonintegral. The valence of a bond (s), measured in valence units (v.u.), is found by distributing the valence (V) of each atom as equally as possible among the bonds it forms. It can be calculated quantitatively by solving Eqs. (1) and (2) for the chosen bond network:

$$V_i = \sum_j s_{ij} \tag{1}$$

$$0 = \sum_{\text{loop}} s_{ij}. \tag{2}$$

The subscripts i and j refer to two bonded atoms. Equation (1), the Valence Sum Rule, ensures that the sum of the bond valences around each atom i is equal to the atomic valence, and Eq.(2), the Equal Valence Rule, ensures that the valence is equally distributed among the bonds (*4, 5*). Since bond valences correlate with bond lengths (*6*), it is possible to predict the length expected for each bond in the compound. Studies of many inorganic structures show that these predictions are close to the distances observed in compounds where bond strain is not expected (*4*).

The first stage in modeling a structure is to predict the bond diagram from the chemical formula and to calculate the expected bond lengths as described above. The second stage involves mapping the bond diagram into Euclidean space. Atoms which are twice bonded in the bond diagram (e.g., Ni and O(2)) must form endless chains in three dimensions. If these chains are extended (rather than looped), they define crystallographic repeat distances. Some crystallographic repeat distances may be determined by more than one set of bonds. For example, in $BaNiGd_2O_5$, the length of the **a** axis is determined independently by the length of the Ni–O(2) bond, the length of the Ba–O(1) bond, and the length of the Gd–O(1) bond. If the lattice translation defined by each of these bonds is to correspond to a common lattice spacing, some bonds must be stretched

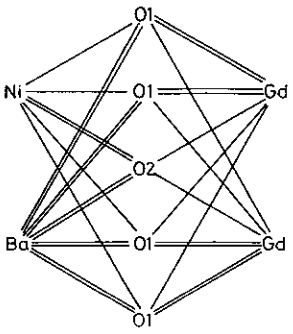

FIG. 2. The bond diagram for $BaNiGd_2O_6$. Each line corresponds to a physically distinct bond. Bond valences (strengths) are not indicated.

TABLE I

COMPARISON OF THE OBSERVED AND PREDICTED STRUCTURES OF $BaNiGd_2O_5$

	Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
Space group		*Immm*	*Immm*		
Cell	*a*	3.787	3.744(1.1)		
	b	5.839	5.780(1.0)		
	c	11.498	11.473(0.2)		
Bonds	Ba–O1 ×8	2.955(4)	2.890(2.1)	2.887(2)	0.068 T
	Ba–O2 ×2	2.919(0)	2.890(1.0)	2.857(2)	0.062 T
	Gd–O1 ×2	2.298(6)	2.282(0.7)	2.421(3)	0.123 C
	Gd–O1 ×4	2.444(4)	2.459(0.6)	2.421(3)	0.023 T
	Gd–O2	2.332(0)	2.382(2.1)	2.408(2)	0.067 C
	Ni–O1 ×4	2.197(6)	2.146(2.3)	2.067(7)	0.130 T
	Ni–O2 ×2	1.894(0)	1.872(1.2)	2.049(6)	0.155 C
Angles	O2–Ni–O2	100	98		
		80	82		
Average difference around	Ba 1.0°, Gd 1.8°				
Valence sums	Ba	1.66(1)	1.95(17)	2.00(20)	
	Gd	2.86(1)	2.78(3)	3.00(5)	
	Ni	1.97(1)	2.17(10)	2.00(2)	
	O1	1.75(1)	1.84(5)	2.00(14)	
	O2	2.34(0)	2.31(1)	2.00(17)	
	R1	0.24	0.19		
Atomic coordinates	Ba	0, 0, 0			
	Gd	0.5, 0, *z*			
		z = 0.7028(0)	0.7076		
	Ni	0.5, 0.5, 0			
	O1	0, *y*, *z*			
		y = 0.7407(10)	0.7573		
		z = 0.3531(5)	0.3585		
	O2	0.5, 0. 0.5			

Notes. Col. 2: Observed structure (*2*) (esd); Col. 3: Modeled structure (% deviation from observed structure); Col. 4: Ideal bond lengths predicted from the bond network using Eq. 1 and 2 (% deviation from observed structure); Col. 5: Observed strain (Col. 2 − Col. 4), C = compression, T = tension. All distances in Å and angles in °.

and others compressed from their ideal predicted lengths. Determining the distribution of strain that best satisfies the chemical requirements is the final step in building the model. This is performed using a least-squares refinement as described in Section 3.

Choices must be made in this procedure. For example, the number of ways in which atoms can be connected to form a bond diagram increases rapidly with the size of the formula unit. Some principle is needed to select only those diagrams that are found to occur in nature. The principle adopted here is the Principle of Maximum Symmetry which states that

> where a choice must be made at a given stage in developing a model, the selection should, as far as possible, retain the symmetry implicit in the previous stage.

Removal of any symmetry operation requires that the environment of two potentially similar atoms be different. One of them will consequently have a higher energy than the other and the net energy of the two atoms cannot therefore be a minimum. Other fac-

tors may, of course, override this effect, stabilizing a lower symmetry structure, but one can only justify dropping a symmetry element if that factor is clearly identified.

There are at least two reasons why symmetry may be broken, resulting in different environments around atoms that would otherwise be expected to be identical: it may not be possible to construct a bond diagram in which all atoms of the same element are equivalent, or it may not be possible to map such a diagram into Euclidean space without destroying the symmetry.

3. Modeling $BaNiGd_2O_5$

The first stage in modeling the structure of $BaNiGd_2O_5$ is to generate the bond diagram (Fig. 2). We start with the nine atoms of the formula unit and assume that each cation has a coordination number close to the average found in known structures. The average coordination number of O around Ni is 5.9, around Ba 10.2, and around Gd 7.4 (*7*). Rounding these to the nearest integer gives expected coordination numbers of 6, 10, and 7 respectively.

To construct the bond diagram, $6 + 10 + 2 \times 7 = 30$ connections must be made between the four cations and five anions, giving the anions an average coordination number of $30/5 = 6$. The choice from among the many possible ways of making these connections is dictated by the Principle of Maximum Symmetry which, in order to maintain the equivalence of the five O atoms, requires that the bonds from each cation be distributed as uniformly as possible among the anions. The ten bonds around Ba are generated, therefore, by assigning two bonds to each O atom. The 6-coordinated Ni forms one bond to each of the five O atoms but it must also form a second bond to one of them. The 7-coordinated Gd atoms each form one bond to three O atoms and two bonds to the other two. With the further constraint that all O atoms have to be 6-coordinate, the only possible diagram is the one given in Fig. 2. Both Gd atoms are equivalent, but the five O atoms are necessarily divided into two groups labeled O(1) and O(2), showing that the bond diagram requires a reduction in the symmetry from that of the formula where all atoms of the same element are assumed to be equivalent.

Ideal bond lengths, shown in Column 4 of Table I, are then predicted from Eqs. (1) and (2) using the method of Ref. (*4*) and the parameters of Ref. (*6*). All the bonds formed by O(2) are predicted to be shorter than the corresponding bonds formed by O(1) as a result of the higher Lewis acidity of the cations bonded to O(1). Although the consequent distortion around Ni is in the right direction, it is much too small to account for the observed bond lengths.

Expanding the network into Euclidean space requires first that the finite bond diagram shown in Fig. 2 be expanded into an infinite bond diagram. For convenience, we start the expansion with the cation having the smallest coordination number (Ni). This forms two bonds with O(2), leading to the expectation that running through the crystal there will be –Ni–O(2)–Ni–O(2)– chains that define one of the axes (**a** = 2x(Ni–O(2)) = 4.10 Å). We then note that O(2) bonds to both of the Gd atoms and to two Ba atoms. We expect these atoms to lie in the plane perpendicular to the –O(2)–Ni–O(2)– chain as shown in Fig. 1. Such an arrangement provides each of these cations with four additional bonds to O(1) (two to the octahedron above and two to the octahedron below). This composite chain contains all the atoms in the formula unit (Ba is included twice), but already there is a problem with commensurability. The **a** axis length is determined not only by the Ni–O(2) bond length, but also by the O(1)–Gd–O(1) and O(1)–Ba–O(1) bond sequences, since the positions of Gd and Ba relative to the axis of the chain are already fixed by the lengths of the Gd–O(2) and Ba–O(2)bonds. As might be expected, the three sets of ideal bond lengths give rise to different expectations for the **a** axis length. The Ni–O bond length requires an axis of 4.10 Å, the Gd–O

bond an axis of 3.28 Å, and the Ba–O bond an axis of 4.12 Å. The observed axis length (3.78 Å) is close to the average of these three values (3.83 Å). In order to be commensurate, the Gd–O(1) bonds must be stretched and the Ni–O(2) and Ba–O(1) bonds compressed. Further, the stretched Gd–O(1) bonds will compress Gd–O(2) and pull the O(1) atoms closer together, reducing the O(1)–Ni–O(1) angle. Already the reasons for both the tetragonal and the orthorhombic distortions around Ni are apparent.

The chains can be combined into the layers shown in Figure 1 by noting that each Ba atom forms two bonds to O(2) and so will form –Ba–O(2)–Ba–O(2)– chains defining a second axis (**b** = 2x(Ba–O(2)) = 5.71 Å). The structure now consists of (001) layers with Gd and O(1) atoms on its surface. These can stack in a way which provides the two remaining Gd–O(1) bonds if adjacent sheets are displaced by $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The resultant structure belongs to space group *Immm* and has **c** ≈ 11.8 Å. This final step breaks the symmetry between the six Gd–O(1) bonds, which split into two crystallographically distinct groups containing four and two bonds respectively.

The bonds along [010] are also strained since the **b** axis is defined both by the Ba–O(2) bonds and the sequence Ni–O(1)–Gd–O(1)–Ni (the Gd atom being in the adjacent layer not shown in Fig. 1). The former corresponds to a **b** axis of length 5.71 Å, the latter of 6.27 Å, with the average (5.99 Å) being close to the observed value (5.84 Å). For the structure to exist, the Ba–O(2) bonds must be stretched from 2.86 Å to around 3.0 Å, which in turn pulls Ba away from the O(1) atoms, causing all the Ba bonds to be stretched, as indicated by the low observed bond valence sum around Ba (1.66 v.u.).

Optimizing these strained distances to give the most chemically acceptable structure is the final stage of modeling. The six free crystallographic parameters (three cell dimensions and three atomic coordinates) are refined against the chemical constraints that need to be satisfied. This was done using the least-squares routine in the program STRUMO (*8*) which, in its current version, offers a choice of quantities that can be minimized, viz: 1. the difference between the bond valence sum and the atomic valence at each atom; 2. the difference between the individual bond valences and the Pauling bond strength of each atom (atomic valence divided by the coordination number, two values per bond); 3. the difference between the bond length and the ideal bond length determined from the bond diagram (Table I, Column 4); 4. the difference between the nonbonding O–O distance within the cation coordination spheres and 3.1 Å. Not all of these quantities are independent; for example, in the absence of bond strain, applying constraint 3 is equivalent to applying constraints 1 and 2 (*5*). The values given in column 3 of Table I were calculated with 5 constraints of type 1 (one for each atom in the asymmetric unit), 60 constraints of type 2 (two for each bond in the formula unit), and 8 constraints of type 4, all constraints given the same weight.

3. Discussion

The cell dimensions and bond lengths of the refined model (Table I, Column 3) differ on average from those observed by 1.2% (maximum 2.3%) and the angles by about 1.5°. The predicted Ba–O and Ni–O bonds are shorter than observed and the Gd–O bonds mostly longer, resulting in rather large differences between the predicted and observed bond valence sums around the cations, but the model accurately predicts the high bond valence sum around O(2) and the low sum around O(I). These result from the compression of the Ni and Gd bonds around O(2) and the stretching of the Ba and Ni bonds around O(1) (Table I, Column 5). Both the tetragonal and the orthorhombic distortions around Ni are well reproduced by the model, and can be seen to arise from the relatively small size of the Gd atom

which both contracts the **a** axis and shortens the O(1)–O(1) contact shared with Ni.

At first sight it is surprising that one can account for the distortion around the Ni atom so effectively using either a crystal packing or an electronic model, but both effects occur and are mutually supportive. The initial source of the distortion lies in the strain introduced along the **a** axis by the need to keep all parts of the structure commensurate. Ni is usually found in the high-spin state with regular octahedral coordination when surrounded by electron withdrawing groups such as O. The energy gained by removing the degeneracy of the *Eg* orbitals is normally too small to overcome the high-spin stabilization energy. In the present structure, the large distortion produced by the geometric strain gives a splitting of the *Eg* levels, further enhanced by the interaction between the d_{z^2} orbitals at O(2), which is large enough to force Ni into the low-spin configuration. The strain energy can be calculated to be about $\frac{1}{3}$ eV per formula unit (making reasonable assumptions about bond force constants), most of the energy being contributed by the distortion at Ni. This is of the same order as the estimate of the electronic stabilization energy (about 1 eV) given by Burdett and Mitchell (*1*).

In the absence of this favorable electronic relaxation the structure would probably be unstable. The degree of instability caused by bond strain can be measured by the strain index, *R*1 in Table I, which is the root-mean-square deviation of the bond valence sums from the atomic valence. In an ideal structure this would be zero, but experimental error leads to values that can be as high as 0.10 v.u. As shown elsewhere (*5*) compounds with a strain index greater than 0.20 v.u. are often found to be unstable at room temperature. In the observed structure the strain index is 0.24 v.u., suggesting that, in the absence of the electronic relaxation, the compound would undergo a displacive transition, probably involving the buckling of the Ni–O(2) chains to distort the environment of the underbonded Ba atom.

Acknowledgment

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