JOURNAL OF SOLID STATE CHEMISTRY 113, 413–419 (1994)

Structures and Crystal Chemistry of Ordered Spinels: $LiFe_5O_8$, $LiZnNbO_4$, and Zn_2TiO_4

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Received November 22, 1993; accepted March 4, 1994

The structures of the title materials have been refined by time-of-flight neutron powder diffraction. $LiFe_5O_8$, $P4_332$, a = 8.3185(1) Å; $LiZnNbO_4$, $P4_322$, a = 6.0804(1), c = 8.3988(1) Å; $ZnTi_2O_4$, $P4_322$, a = 5.9927(1), c = 8.4266(2) Å. All three materials have structures that are ordered derivatives of the ideal spinel structure. Bond lengths are analyzed in terms of bond valences. Modifications to the "equal valence rule" [I. D. Brown, *Acta Crystallogr. Sect. B* 35, 1305 (1977)] for predicting bond lengths in crystals are shown to be necessary in oxides of early transition elements.

INTRODUCTION

In the "normal" spinel structure of ternary oxides AB_2O_4 the A atoms are in tetrahedral coordination and the B atoms are in octahedral coordination by oxygen. In a commonly used convention these are written $A[B_2]O_4$, with the brackets enclosing the octahedrally coordinated metal atoms. It has long been recognized that many chemically ternary compositions have an "inverse spinel" structure $B[AB]O_4$ with A and B apparently disordered over the octahedral sites. As there are (at least) two kinds of B atoms in the structure, these compounds are better considered as quaternary oxides. Closer examination of annealed samples of inverse spinels have shown in some instances that the A and B atoms on octahedral sites order to produce structures of lower symmetry than the parent "normal" spinel. Although spinels have been very extensively studied for decades, there have been very few *quantitative* structural studies of ordered "inverse" spinels; indeed the only such study of the AB_2O_4 composition of which we are aware is that of $Li[LiTe]O_4$ (1) although Li_2WO_4-II has been reported (2) to have a related, but different, structure. Cation ordering has also been studied in $LiFe_5O_8$ = $Fe[Li_{0.5}Fe_{1.5}]O_4$, and in this instance a quantitative crystal structure has also been reported (3). The presence of ordering in well-annealed $Zn[LiNb]O_4$ (4) and $Zn[ZnTi]O_4$ (5) has been established and *qualitative* structures have been proposed, although the difficulty of obtaining single crystals has so far precluded a quantitative study.

It has been suggested (6) that the bond lengths in "inverse spinels" should provide a good test of the bond valence method of analyzing bond lengths in oxides, and in particular a good test of the Brown (7) "equal valence rule" for predicting bond lengths. Accordingly we have undertaken a quantitative determination of the structures of Zn_2TiO_4 and $LiZnNbO_4$ by time-of-flight (TOF) neutron powder diffraction. We have also redetermined the structure of $LiFe_5O_8$ by the same method and find a structure in good agreement with that previously reported (3). Bond lengths in the resulting structures are subject to analysis by the bond valence method. The results indicate that the equal valence rule requires modification before application to oxides that contain early transition metals in their maximum oxidation state [such as Ti(IV) and Nb(V)].

EXPERIMENTAL

Sample preparation. The spinels were made by grinding together stoichiometric amounts of the binary component oxides and Li_2CO_3 and heating in air. The heating schedule for $LiFe_5O_8$ was 5 days at 900°C, followed by an anneal for 7 days at 700°C. $LiZnNbO_4$ was heated at 1000°C for 7 days followed by an anneal for 4 weeks at 700°C. A large preparation of disordered (cubic) Zn_2TiO_4 was obtained by heating for 7 days at 1000°C. Separate samples were then annealed at 400, 450, 500, 550, and 600°C for 16 weeks. Ordering could be detected by splitting of the lines of the initially cubic X-ray diffraction pattern and the sample annealed at 450°C was judged to be the best ordered and used for subsequent neutron diffraction analysis. The Zn_2TiO_2 was possibly slightly nonstoichiometric due to loss of ZnO in the initial firing as a trace of TiO_2 impurity was detected in the annealed sample. The exigencies of scheduling neutron diffraction did not allow us time to prepare a new annealed sample. The other materials were found to be single phase by X-ray powder diffraction. Earlier work (3) had found that $LiFe_5O_8$ disordered above 755°C but we found no discern-

0022-4596/94 $6.00

TABLE 1
Number of Variables Refined and Agreement Indices

	$LiFe_5O_8$	$LiZnNbO_4$	Zn_2TiO_4
Variables	59	46	51
R_p	5.8%	2.6%	3.8%
R_{wp}	6.5%	3.8%	4.3%
χ^2	3.6	2.5	2.5

ible difference between the X-ray diffraction patterns of the sample prepared at 900°C and that subsequently annealed at 700°C, both of which corresponded to the fully ordered phase.

Neutron diffraction. TOF neutron diffraction data were collected at 305 K for $LiFe_5O_8$ on the neutron powder diffractometer (NPD) at the Manuel Lujan Jr. Neutron Scattering Center at Los Alamos National Laboratory (LANSCE). Data were collected at ±90 and ±148° 2θ. Data for $LiNbZnO_4$ and Zn_2TiO_4 were collected on the high intensity powder diffractometer (HIPD) at LANSCE, at 305 K. Data were collected at ±153.4 and ±90.0° 2θ.

Structure refinements. Structure refinements were done using the general structure analysis system (GSAS) of Larson and Von Dreele (8). Atom positions were initially set at positions corresponding to the ideal cubic spinel structure. Refinements were begun by first refining a 12-coefficient background function and a scale factor for each data set. Next, lattice parameters were refined, then the peak-shape function (profile) coefficients, α_1, β_0, β_1, and σ_1. The final refinement included atom fractions (site occupancies), atom positions, and thermal parameters. For $LiNbZnO_4$ and Zn_2TiO_4, only isotropic thermal parameters were refined, but anisotropic thermal parameters were refined for $LiFe_5O_8$. Factors correcting zero-point error and absorption were also refined.

We were particularly interested in determining the degree of Nb, Li ordering in $LiNbZnO_4$ and Zn, Ti ordering in Zn_2TiO_4 so the neutron scattering lengths (b in fm) are of interest. These are (9) Li, −1.9, Zn, 5.7; Ti, −3.3; Nb, 7.1; so it may be seen that neutron diffraction is eminently suitable for this purpose. In $LiZnNbO_4$ the site occupancy of the majority component refined to 98(2)% indicating essentially perfect order. The corresponding result in Zn_2TiO_4 is 92(4)% so that a small degree of residual disorder cannot be ruled out in this case.

Table 1 lists the number of variables refined and the final R_p, R_{wp}, and χ^2 for each material and Tables 2–4 report the structural parameters and isotropic thermal parameters, U_{iso}, for the three materials. Structure amplitudes are given in Table 5.[1] Observed and calculated intensity profiles for one detector bank are shown in Fig. 1 for $LiZnNbO_4$ and in Fig. 2 for Zn_2TiO_4.

TABLE 3
Structural Parameters[a] for $LiZnNbO_4$

Atom	Site	x	y	z	$100U_{iso}$ (Å^2)
Li	4a	0.2254(9)	0	$\frac{1}{4}$	2.1(1)
Zn	4c	0.2619(2)	0.2619(2)	$\frac{5}{8}$	0.46(2)
Nb	4b	$\frac{1}{2}$	0.2156(2)	0	0.11(2)
O(1)	8d	0.2637(1)	0.0186(1)	0.9951(1)	0.57(2)
O(2)	8d	0.2679(1)	0.4794(1)	0.0172(1)	0.32(2)

[a] Space group $P4_322$, a = 6.0804(1) Å, c = 8.3988(1) Å.

DISCUSSION OF THE STRUCTURES

$LiFe_5O_8$. Our structure determination is in excellent agreement with the earlier determination (3) which is gratifying as very different techniques (single crystal X-ray and powder neutron diffraction, respectively) were used in the two studies. The bond lengths determined in the two cases differ on average by 0.004 Å (worst case 0.009 Å). The standard deviations reported for the X-ray study were ±0.003 Å and less than ±0.001 Å in the present work so we may consider this structure to be rather well determined.

TABLE 2
Structural Parameters[a] for $LiFe_5O_8$

Atom	Site	x	y	z	$100U_{iso}$ (Å^2)
Li	4b	$\frac{5}{8}$	$\frac{5}{8}$	$\frac{5}{8}$	2.3(2)
Fe(1)	8c	0.9981(1)	0.9981(1)	0.9981(1)	0.33(1)
Fe(2)	12d	$\frac{1}{8}$	0.3674(1)	0.8826(1)	0.31(3)
O(1)	8c	0.3849(1)	0.3849(1)	0.3849(1)	0.39(3)
O(2)	24e	0.1169(1)	0.1272(1)	0.3835(1)	0.43(3)

[a] Space group $P4_332$, a = 8.3195(1) Å.

TABLE 4
Structural Parameters[a] for Zn_2TiO_4

Atom	Site	x	y	z	$100U_{iso}$ (Å^2)
Zn(1)	4a	0.2580(9)	0	$\frac{1}{4}$	0.65(3)
Zn(2)	4c	0.2545(3)	0.2545(3)	$\frac{5}{8}$	0.52(2)
Ti	4b	$\frac{1}{2}$	0.2361(2)	0	0.73(2)
O(1)	8d	0.2648(4)	0.0307(3)	0.0004(3)	0.85(4)
O(2)	8d	0.2551(4)	0.4867(3)	0.0173(2)	0.96(3)

[a] Space group $P4_322$, a = 5.9927(2) Å, c = 8.4266(2) Å.

[1] Deposited data.

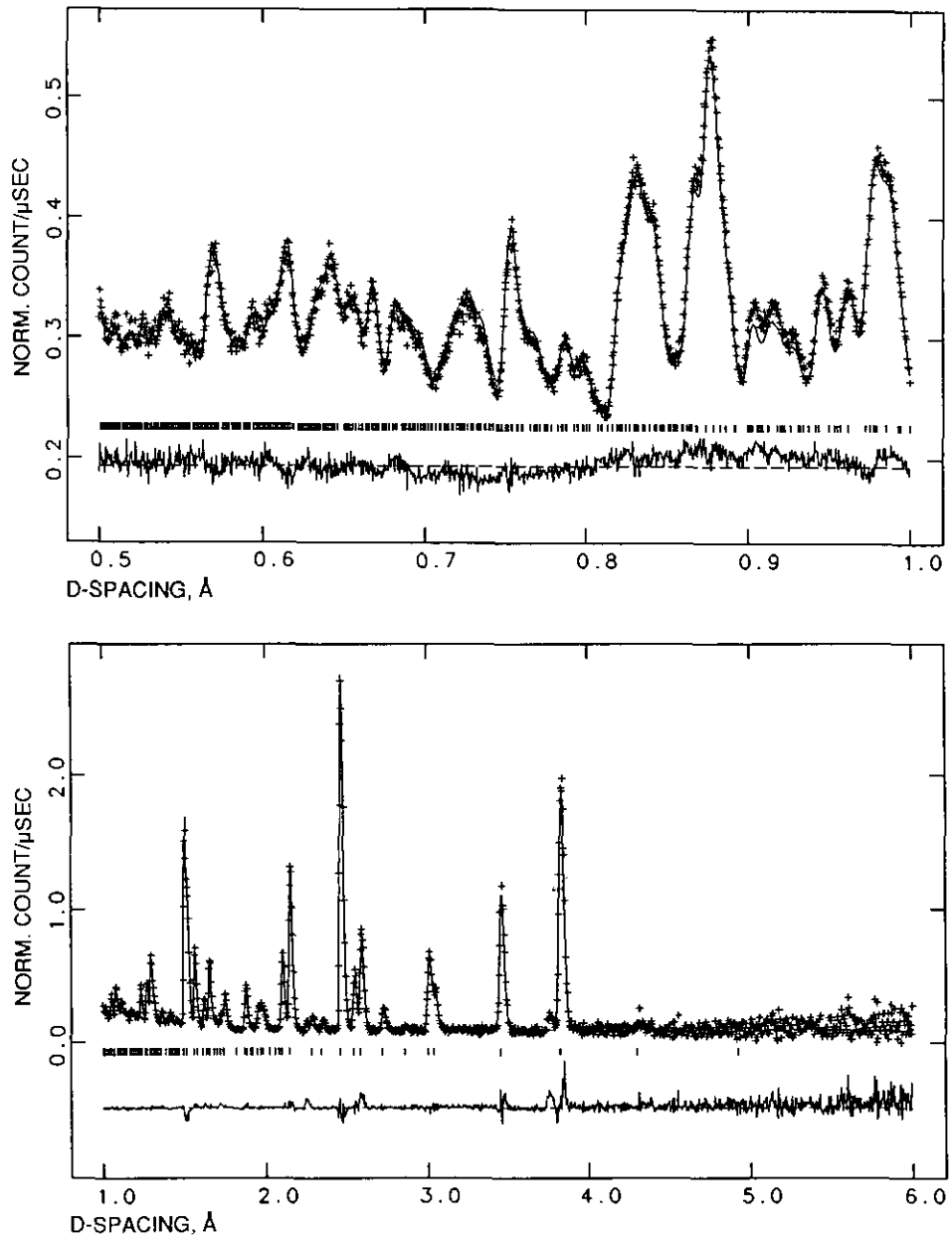

FIG. 1. Neutron diffraction profile fit for $LiZnNbO_4$. Data points are shown a "+," and the solid line is the calculated profile. The tick marks indicate the expected positions of Bragg reflections. The difference curve shown below the profile is on the same scale. The background has been subtracted.

We focus the discussion on the observed and predicted bond lengths in the structure. Li is in a site of 32 (D_3) symmetry and bonded to six O(2) atoms. The symmetry requires that all the Li–O bonds are of equal length. Fe(1) in a site of 3 (C_3) symmetry is bonded to one O(1) and three O(2) oxygen atoms in a distorted tetrahedron (note that in normal spinels the tetrahedral atom is constrained to be in a regular tetrahedron) and Fe(2) in a site of 2 (C_2) symmetry is bonded to two O(1) atoms and four O(2) atoms in a distorted octahedron.

The qualitative nature of the bond length variations expected can be seen by examining the Pauling electrostatic bond strength sums at the anions. These are 2.25 at O(1) and 1.917 at O(2). As O(1) is "overbonded" and O(2) "underbonded" one expects the Fe–O(1) bonds to be longer than the Fe–O(2) bonds. Brown (7) first suggested how the bond valence method could be used to make a quantitative prediction of expected bond lengths in such circumstances and a slight modification of his method that is more suitable for cases where average bond

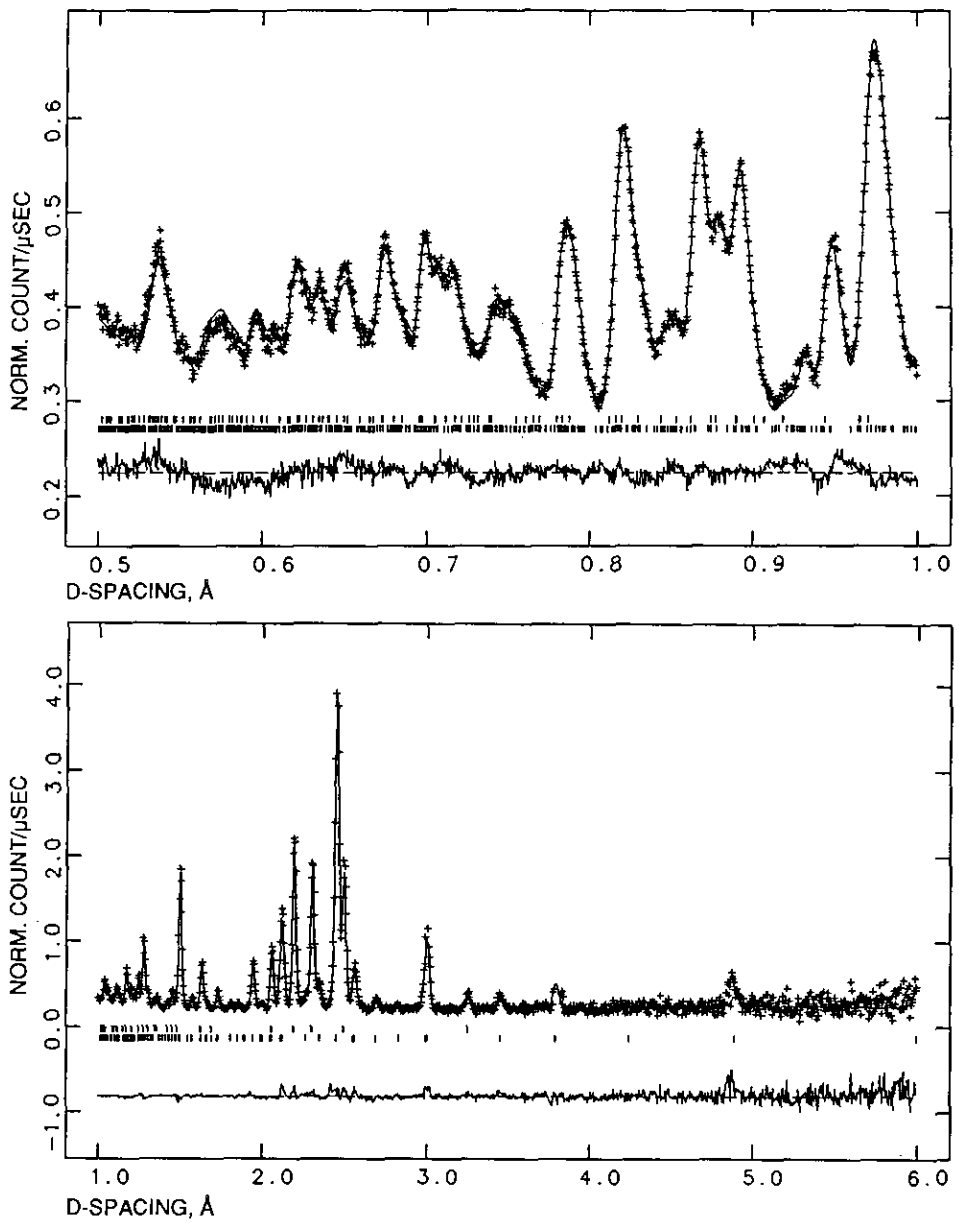

FIG. 2. Neutron diffraction profile fit for Zn_2TiO_4. Data points are shown as "+," and the solid line is the calculated profile. The lower set of tick marks indicate the expected positions of Bragg reflections for the major phase and the upper set of tick marks represent the positions of the trace of rutile TiO_2 in the preparation. The difference curve shown below the profile is on the same scale. The background has been subtracted.

valences differ considerably was subsequently described (10). The latter method, which is fully documented elsewhere (10, 11),[2] weights the requirement that valences be as nearly equal as possible by the average valence of each type of bond. In the present instance the average valences range from $\frac{1}{6}$ for Li–O bonds to $\frac{3}{4}$ for Fe(1)–O bonds, but as Li is bonded to only one kind of atom, the valences of Li–O bonds are predicted to be the same ($\frac{1}{6}$) using either method, and the predicted valences for Fe–O differ only inconsequentially in the two methods. Table 6 lists predicted valences calculated as described above, bond lengths calculated for these valences from published bond valence parameters (12), and observed bond lengths in $LiFe_5O_8$. The agreement is very good and clearly an improvement over methods that use sums of radii which would predict that all bonds from Fe(1) and all bonds from Fe(2) are equal in length.

[2] The reader unfamiliar with the bond valence method will find a tutorial account in (11).

TABLE 6
Predicted Valences and Calculated and Observed Bond Lengths in $LiFe_5O_8$

Bond	Valence	d_{calc}	d_{obs}
Li–O(2)	0.167	2.13	2.10
Fe(1)–O(1)	0.660	1.91	1.92
Fe(1)–O(2)	0.780	1.85	1.88
Fe(2)–O(1)	0.447	2.06	2.06
Fe(2)–O(2)	0.527	2.00	1.98[a]

[a] Average.

$LiZnNbO_4$. Our structure determination shows that the proposed (4) cation ordering was correct and that $Zn[LiNb]O_4$ is isostructural with $Li[LiW]O_4$ (1). The pattern of ordering of octahedral sites is illustrated in Fig. 3 where it is compared with the pattern originally proposed (13) for ordering of Fe(II) and Fe(III) in Fe_3O_4 (magnetite). These two patterns are probably the simplest that comply with the "Anderson condition" (14) that charge ordering on octahedral sites will be such that each tetrahedron of sites (see Fig. 3) will consist of two of each kind of charge. It should be remarked that the ordering in the low-temperature (charge-ordered) form of magnetite is considerably more complex (15).

If we disregard the Li, Nb ordering, the structure is the familiar spinel structure [see e.g., (16)]. However if we consider just the stronger bonds (Zn–O) and Nb–O) the structure has some features of interest. Edge-sharing NbO_6 octahedra form helical (4_3) rods with their axes parallel to the c-axis; these rods are cross-linked by ZnO_4 tetrahedra to form a three-dimensional framework. Figure 4 illustrates a fragment of the structure illustrating this aspect. In a cubic spinel with the same volume, $a = 8.53$ Å and the distance between octahedral sites is $a/\sqrt{8} = 3.02$ Å. Further if the O atoms were in ideal cubic close packing this would also be the distance between O atoms.

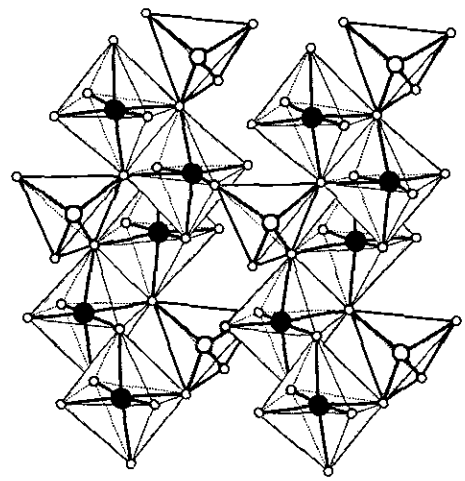

FIG. 4. A fragment of the structure of $LiZnNbO_4$ structure showing two helices of edge-sharing NbO_6 octahedra and their mode of linkage by ZnO_4 tetrahedra. Large filled circles are Nb atoms and small open circles are O atoms. The c-axis is vertical.

In $LiZnNbO_4$ the shortest Li···Li distance is 2.86 Å and the shortest Nb···Nb distance is 3.22 Å. The O···O distances exhibit a wider range: from 2.57 to 3.28 Å.

One of the first things one should do after refining a structure is to determine the *apparent* valences of the atoms as calculated from the observed bond lengths. These were calculated using published bond valence parameters (12) and are listed in Table 7 for the structure of $LiZnNbO_4$. The close agreement with expected valences leads us to believe that the structure is not significantly in error. Table 7 also lists the observed metal–oxygen bond lengths in $LiZnNbO_4$. As for $LiFe_5O_8$, and for similar reasons, the metal–oxygen bond lengths in the various polyhedra are not equal.

The expected bond lengths were calculated in the manner described above for $LiFe_5O_8$. Comparison of the calculated values (column 3 in Table 8) with observed values shows that the bond lengths are correctly ordered, but

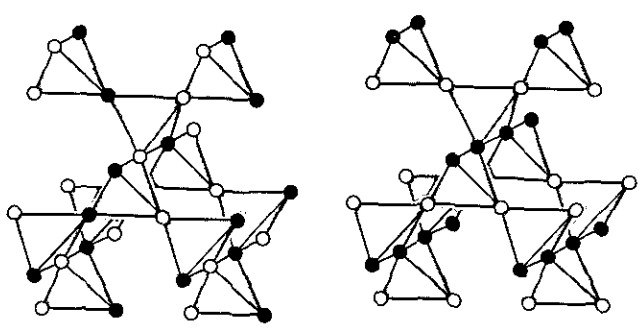

FIG. 3. Left: the tetragonal pattern of ordering of Li and Nb on spinel octahedral sites. Right: the orthorhombic pattern of ordering of octahedral sites proposed by Verwey *et al.* (13) for magnetite.

TABLE 7
Valences[a] and Bond Lengths in $LiZnNbO_4$

Atom	Valence	To atom	Bond lengths (Å)
Li	0.98	O(1)	2.038(3) (2×), 2.157(1) (2×)
		O(2)	2.249(4) (2×)
Zn	1.91	O(1)	1.981(1) (2×)
		O(2)	1.976(1) (2×)
Nb	4.94	O(1)	1.872(1) (2×)
		O(2)	2.141(1) (2×), 1.985(1) (2×)
O(1)	1.96		
O(2)	1.97		

[a] Calculated as bond valence sums from the observed bond lengths.

TABLE 8
Predicted Valences and Calculated and Observed Bond Lengths in $LiZnNbO_4$

Bond	Valence[a]	d_{calc}[a]	Valence[b]	d_{calc}[b]	d_{obs}
Li–O(1)	0.185	2.09	0.195	2.07	2.10[c]
Li–O(2)	0.126	2.23	0.111	2.28	2.25
Zn–O(1)	0.59	1.90	0.5	1.96	1.98
Zn–O(2)	0.41	2.04	0.5	1.96	1.98
Nb–O(1)	1.04	1.90	1.12	1.87	1.87
Nb–O(2)	0.73	2.03	0.69	2.05	2.06[c]

[a] Weighting bonds by average valence.
[b] Making Zn–O bonds equal and with equal weights for Li–O and Nb–O bonds.
[c] Average.

TABLE 10
Predicted Valences and Calculated and Observed Bond Lengths in Zn_2TiO_4

Bond	Valence	d_{calc}	d_{obs}
Zn(1)–O(1)	0.354	2.09	2.10[a]
Zn(1)–O(2)	0.293	2.16	2.06
Zn(2)–O(1)	0.545	1.93	2.01
Zn(2)–O(2)	0.455	2.00	1.96
Ti–O(1)	0.747	1.92	1.87
Ti–O(2)	0.626	1.99	2.06[a]

[a] Average.

the method overestimates the range of Zn–O bond lengths and underestimates the range of Nb–O bond lengths. The reason for this is in fact well understood (6, 11). Bonds to oxygen from transition elements in their maximum oxidation states [such as Nb(V)] are unusually compliant and distorted environments are common (as in oxide ferroelectrics), yet the method considers the Nb–O bonds of average valence $\frac{5}{6}$ to be "stiffer" than the Zn–O bonds of average valence $\frac{1}{2}$. To allow for the easy deformability of the Nb–O bonds, the calculation was repeated with the Zn–O bond valences fixed at $\frac{1}{2}$ and the Li–O bonds (average valence $\frac{1}{6}$) and Nb–O bonds treated on an equal footing. The calculated bond lengths (column 5 in Table 8) are now rather close to the observed values; the average deviation of the calculated bond lengths from those observed is reduced from 0.038 to 0.018 Å.

Zn_2TiO_4. The structure is very similar to that of $LiZnNbO_4$ with Zn(1) in octahedral coordination and Zn(2) in tetrahedral coordination. Bond lengths and apparent valences are listed in Table 9; again the apparent atomic valences are close to those expected and the coordination polyhedra are distorted. In Table 10, observed bond lengths are recorded and compared with those calculated using the bond valence method with bonds weighted according to their average valences. The most obvious discrepancies are that the variations in Zn–O bond lengths are overestimated and that the variations in Ti–O bond lengths are underestimated suggesting that the stiffness of the latter bonds has been overestimated as for Nb–O bonds in $LiZnNbO_4$. Again this result is not unexpected for bonds from Ti(IV) to oxygen (6, 11). As noted above, the material studied might be slightly nonstoichiometric due to loss of ZnO in preparation.

TABLE 9
Valences[a] and Bond Lengths in Zn_2TiO_4

Atom	Valence	To atom	Bond lengths (Å)
Zn(1)	2.13	O(1)	2.091(4) (2×), 2.112(2) (2×)
		O(2)	2.059(4) (2×)
Zn(2)	1.88	O(1)	2.010(3) (2×)
		O(2)	1.960(3) (2×)
Ti	3.96	O(1)	1.872(6) (2×)
		O(2)	1.996(2) (2×), 2.105(6) (2×)
O(1)	2.01		
O(2)	1.98		

[a] Calculated as bond valence sums from the observed bond lengths.

CONCLUSIONS

The crystal structure of $LiFe_5O_8$ has been confirmed. The bond lengths calculated using a modification (10) of the Brown (7) bond valence method are in excellent agreement with those observed (average deviation 0.015 Å). The crystal structure of $LiZnNbO_4$ confirms the pattern of (Li, Nb) ordering originally (4) proposed for this material. Zn_2TiO_4 is isostructural. A similar bond valence analysis of the last two structures suggests that an improved match with experiment could be obtained by allowing for the easy deformability of Ti(IV)–O and Nb(V)–O bonds. We suggest that a way to do this is to analyze a larger number of oxide structures containing these, and related, cations to determine optimum weights for such bonds. One might expect that these weights would correlate with other measures of "stiffness" such as bond-stretching force constants. The utility of such data in empirical modeling of oxide crystal structures should be apparent.

ACKNOWLEDGMENTS

This work was supported by Grant DMR 91 20191 from the National Science Foundation. We have benefited from the use of facilities at the Manuel Lujan, Jr. Neutron Scattering Center, a national user facility, funded as such, by the DOE/Office of Basic Energy Sciences.

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