New formula for lattice dimension of an oxide spinel with cubic structure

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Abstract. An empirical relation between lattice parameter and cationic radii for cubic spinels has been established by considering the packing of anions in non-ideal situation and ionic displacement parameter ($\delta = u - 3/8$). This relation gives the value of a, the lattice parameter, which is much closer to the observed value.

Keywords. Lattice dimension; oxide spinel; cubic structure; cationic radii.

1. Introduction

Oxide spinels, whose properties depend on the valence and site distribution of the cations, have wide range of applications. The cationic distribution can be estimated from site preference energies, size of the ions, type of bonds, diffraction line intensities, etc. Considering divalent ionic radius of oxygen to be 1·40 Å, Mikheev (1955) gave an empirical relation to determine the lattice parameter a as

$$a = 5·778 + 0·95\, r_a + 2·79\, r_b,\tag{1}$$

where r_a and r_b are the tetrahedral and octahedral cationic radii respectively. Equation (1) is based on Goldschmidt (1935) ionic radii. This relation, though helps in understanding the site distribution (Somenkov 1964), does not yield values that match very closely with the experimental results. Moreover, it does not take care of the coordination polyhedra and the spin states of the cations.

Azaroff (1977) discussed the dependence of unit cell dimensions of crystalline solids upon the constituent ions in specific arrangement and packing. Many have attempted to determine the absolute values of ionic radii which depend only on the valency of ions (Goldschmidt 1935; Pauling 1939; Ahrens 1952; Sanderson 1967). Shannon and Prewitt (1969, 1970), in addition to the valency of ions, considered the influence of the coordination polyhedra and spin states. We therefore thought it worthwhile to establish a relation between ionic radii and lattice parameter of a cubic spinel.

In cubic spinel, A site ion has a coordination number 4. The ionic displacement parameter δ, is correlated with r_a and r_o, the ionic radii of cations at A site and the oxygen anions respectively. The lattice parameter a is then calculated in terms of δ, r_a, r_b and r_o. In the spinel structure AB_2O_4, there are two or more types of metal atoms linked to the oxygen atom either tetrahedrally or octahedrally. The former is usually referred to as A-site and the latter as B-site. The cation at A-site is surrounded by 4 oxygen ions while each oxygen ion is surrounded by 4 cations, of which one is from A-site and the remaining three from B-site. Hence, even though the oxygen ion is tetrahedrally coordinated, the first coordination sphere of oxygen is influenced by distances of B–O type of bond. Therefore it is appropriate to take $r_o = 1·40$ Å which is oxygen ion radius for six-coordination as given by Shannon and Prewitt (1969).

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On substituting for δ in terms of r_a and r_o, we get the relation between a, r_a and r_b which is independent of δ (derivation of the relation is given in appendix). The relation obtained is:

$$a = \{(r_a/\sqrt{3} + r_b + 2 \cdot 0951 r_o) + [(r_a/\sqrt{3} + r_b + 2 \cdot 0951 r_o)^2$$
$$- 1 \cdot 866(1 \cdot 3333 r_a^2 + 0 \cdot 0675 r_o^2 - 0 \cdot 6 r_a r_o)]^{1/2}\}/0 \cdot 933,$$

where r_a and r_b are the tetrahedral and octahedral cationic radii respectively. We have used the above relation to calculate the lattice parameter a in the well-known compounds with definite valencies and site distributions.

2. Results and discussion

Table 1 gives the calculated values of lattice parameter a for some oxide spinels using our formula and employing the values of ionic radii given by Shannon and Prewitt (1969, 1970). For comparison, in table 1 are also given the values of a calculated by

Table 1. Observed and calculated lattice parameters.

Spinels	Ion at A-site	Observed $a(\text{Å})$	Calculated by Mikheev's formula $a(\text{Å})$	Calculated by Authors' formula $a(\text{Å})$
$CdAl_2O_4$	Cd^{2-}	8·137	8·017	8·333
$CdCr_2O_4$	Cd^{2+}	8·467	8·240	8·506
$CdFe_2O_4$	Cd^{2+}	8·690	8·324	8·571
$CdGa_2O_4$	Cd^{2+}	8·390	8·268	8·528
$CdMn_2O_4$	Cd^{2+}	8·220	8·156	8·441
CdV_2O_4	Cd^{2+}	8·695	8·323	8·571
$FeCoCrO_4$	Fe^{3+}	8·340	8·127	8·330
$FeCr_2O_4$	Fe^{2+}	8·340	8·078	8·341
$FeCuMnO_4$	Fe^{3+}	8·340	8·169	8·363
$FeMnNiO_4$	Fe^{3+}	8·360	8·112	8·319
FeV_2O_4	Fe^{2+}	8·550	8·162	8·405
$GeFe_2O_4$	Ge^{4+}	8·420	8·334	8·452
$MgAl_2O_4$	Mg^{2+}	8·086	7·808	8·117
$MgCo_2O_4$	Mg^{2+}	8·107	7·779	8·095
$MgCr_2O_4$	Mg^{2+}	8·322	8·031	8·289
$MgFe_2O_4$	Mg^{2+}	8·352	8·115	8·353
$MgGa_2O_4$	Mg^{2+}	8·260	8·059	8·310
$MgMn_2O_4$	Mg^{2-}	8·080	7·947	8·224
MgV_2O_4	Mg^{2-}	8·416	8·114	8·353
$MnCoFeO_4$	Mn^{2+}	8·410	8·033	8·413
$MnCrNiO_4$	Mn^{3+}	8·390	8·142	8·375
Mn_2NiO_4	Mn^{3+}	8·420	8·198	8·461
$MnNi_2O_4$	Mn^{4+}	8·380	8·216	8·418
$ZnAl_2O_4$	Zn^{2+}	8·086	7·827	8·138
$ZnCo_2O_4$	Zn^{2+}	8·047	7·798	8·116
$ZnCr_2O_4$	Zn^{2+}	8·312	8·050	8·310
$ZnFe_2O_4$	Zn^{2+}	8·440	8·134	8·374
$ZnGa_2O_4$	Zn^{2+}	8·370	8·078	8·331
$ZnMn_2O_4$	Zn^{2-}	8·077	8·970	8·245
ZnV_2O_4	Zn^{2+}	8·409	8·133	8·374

Underlined values show closeness to the observed one.

Table 2. Suitable spin states from observed lattice parameter.

$Mg^{2+}[Mn_2^{3+}]O_4^{2-}$	$Mg^{2+}[Co_2^{3+}]O_4^{2-}$
L	L
$Zn^{2+}[Mn_2^{3+}]O_4^{2-}$	$Zn^{2+}[Co_2^{3+}]O_4^{2-}$
L	L
$Cd^{2+}[Mn_2^{3+}]O_4^{2-}$	$Mg^{2+}[Fe_2^{3+}]O_4^{2-}$
L	H
$Mn^{3+}[Mn^{3+}Ni^{2+}]O_4^{2-}$	$Zn^{2+}[Fe_2^{3+}]O_4^{2-}$
H	H
$Fe^{3+}[Mn^{3+}Ni^{2-}]O_4^{2-}$	$Cd^{2+}[Fe_2^{3+}]O_4^{2-}$
H	H
$Fe^{3+}[Mn^{3+}Cu^{2+}]O_4^{2-}$	$Ge^{4+}[Fe_2^{2+}]O_4^{2-}$
H	H

L, low spin state, H, high spin state

Mikheev's formula by using values of ionic radii as given by Shannon and Prewitt (1969, 1970). A close observation of the table shows that the values of lattice parameter calculated by our formula are, in general, closer to the experimental results. The values of lattice parameter have also been calculated using the ionic radii given by Goldschmidt (1935), Pauling (1939), Ahrens (1952) and Sanderson (1967). However these values are not included in the table, since they differ widely from the values determined experimentally.

The values given in table 1 are accounted for low as well as high spin cationic states. It is seen from table 2 that for cation Mn^{3+} existing at the B site, just low or high spin ionic radii do not fit well in all the compounds. It is found that when Mn^{3+} ion is present along with a divalent neighbour at B site, the high spin ionic radius is more suitable, while in the case of trivalent neighbour only the low spin ionic radius appears to suit well. The agreement in the case of high spin state is not surprising although uncommon for low spin states (table 2).

3. Conclusions

The relation given by us can be used to calculate the lattice parameter of oxide cubic spinels. It will also be a useful tool to decide the probable degree of inversion in the distribution of cations in the newly synthesized spinels.

Appendix

Derivation of relation for the lattice parameter a:

Tetrahedral and octahedral bond lengths R_A and R_B in the cubic spinel are given as

$$R_A = a\sqrt{3}\left(\frac{1}{8} + \delta\right) \text{ and } R_B = a\left(\frac{1}{16} - \frac{\delta}{2} + 3\delta^2\right)^{1/2}$$

The above equations give

$$a = \frac{R_A + R_B}{\sqrt{3}\left(\frac{1}{8} + \delta\right) + \left(\frac{1}{16} - \frac{\delta}{2} + 3\delta^2\right)^{1/2}} \qquad (A1)$$

Let

$$D = \sqrt{3}\left(\frac{1}{8} + \delta\right) + \left(\frac{1}{16} - \frac{\delta}{2} + 3\delta^2\right)^{1/2} \tag{A2}$$

The second term of D can be simplified as follows

$$\left(\frac{1}{16} - \frac{\delta}{2} + 3\delta^2\right)^{1/2} = 1/4(1 - 8\delta + 48\delta^2)^{1/2}$$

$$= 1/4[1 - 8\delta(1 - 6\delta)]^{1/2}.$$

Using binomial expansion and neglecting higher powers of δ we get

$$\left(\frac{1}{16} - \frac{\delta}{2} + 3\delta^2\right)^{1/2} = (1/4) - \delta + 4\delta^2. \tag{A3}$$

Putting (A3) in (A2) we get

$$D = (\sqrt{3}/8) + \sqrt{3}\delta + (1/4) - \delta + 4\delta^2 \tag{A4}$$

Consider that the anions are occupying four alternate corners of the cube of side a and that the cation is at the centre. If r_a is the radius of the sphere representing tetrahedral void (cation) and r_x the radius of the (anion) sphere in the closest packing, we then have

$$r_x = (\sqrt{2}/2)a \text{ and } r_a + r_x = (\sqrt{3}/2)a$$

Therefore $r_a/r_x = (\sqrt{3/2}) - 1 = 0.225$. Thus for ideal ionic packing the allowed ionic radius for any ion of radius r_a is given as $0.225r_x$. In non-ideal situation, the expression would be $a\sqrt{3}\,\delta = r_a - 0.225r_x$, where $\delta = (u - 3/8)$ is ionic displacement parameter. In an ideal packing $u = 3/8$. In non-ideal packing $u > 3/8$ and the anion will move along the body diagonal of the cube. In that case

$$\delta = \left(\frac{r_a - 0.225r_x}{\sqrt{3}a}\right)$$

For oxygen ion $r_x = r_o$, hence

$$\delta = \left(\frac{r_a - 0.225r_o}{\sqrt{3}a}\right). \tag{A5}$$

Substituting the value of δ in expression (A4), we get

$$D = \frac{\sqrt{3}}{8} + \sqrt{3}\left(\frac{r_a - 0.225r_o}{\sqrt{3}a}\right) + \frac{1}{4} - \left(\frac{r_a - 0.225r_o}{\sqrt{3}a}\right) + 4\left(\frac{r_a - 0.225r_o}{\sqrt{3}a}\right)^2. \tag{A6}$$

Now $R_A = r_a + r_o$ and $R_B = r_b + r_o$. Therefore $R_A + R_B = r_a + r_b + 2r_o$. From (A1)

$$a = (R_A + R_B)/D = (r_a + r_b + 2r_o)/D,$$

Therefore

$$r_a + r_b + 2r_o = Da \tag{A7}$$

Putting the value of D from (A6) in (A7) and simplifying we get

$$0.4665a^2 - (r_a/\sqrt{3} + r_b + 2.0951r_o)a + (1.3333r_a^2 + 0.0675r_o^2 - 0.6r_ar_o) = 0.$$

Taking positive root, we get

$$a = \{(r_a/\sqrt{3} + r_b + 2\cdot0951r_o) + [(r_a/\sqrt{3} + r_b + 2\cdot0951r_o)^2$$
$$- 1\cdot866(1\cdot3333r_a^2 + 0\cdot0675r_o^2 - 0\cdot6r_a r_o)]^{1/2}\}/0\cdot933.$$

References

Ahrens 1952 *Geochim. Cosmochim. Acta* **2** 155
Azaroff L V 1977 in *Introduction to solids*, (Bombay: Tata-McGraw-Hill) p. 67
Goldschmidt V M 1935 in *International Tobellen Zur Bestimmung Van Kristallstrukture*
Mikheev V J 1955 *Dokl. Akad. Nauk SSSR* **101** 343
Pauling L 1939 *Nature of chemical bond*, (New York: Cornell University Press) 2nd Ed. p. 346
Sanderson R T 1967 *Inorganic chemistry* (New York: Reinhold Publishing Corporation) p. 136
Shannon R D and Prewitt C T 1969 *Acta Crystallogr.* **B25** 925
Shannon R D and Prewitt C T 1970 *Acta Crystallogr.* **B26** 1046
Somenkov V A 1964 *Fiz metal metalloved* **18** 853