DEFECT FORMATION IN SPINELS IN OXYGEN NONSTOICHIOMETRY
(a review)

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This paper discusses the nonstoichiometry and the related pattern of defect formation in spinels — substances widely used in the various fields of science and technology.

A typical ordered spinel is a ternary chemical compound of general formula $\text{A}^{2+}\text{B}^{3+}\text{O}_4$. It has two cations, one with an oxidation state of $2^+$, and the other, $3^+$ (here, A and B are the symbols of these cations). The core of the spinel structure is a face-centered cube with all of its corners occupied by oxygen atoms (Fig. 1). Assuming that the crystal structure consists of polyhedra, two kinds of voids can be readily discerned inside the cube, which might be assigned the shape of an octahedron and a tetrahedron, respectively. A fragment (one-eighth of a unit cell) of the schematic spinel structure based on such an assumption is shown in the accompanying figure. To avoid overcrowding, the figure shows only one octahedron and one tetrahedron.

Some of these polyhedra can be occupied by the cation components of the spinel — elements A and B. When all of their nodes are occupied by oxygen atoms, the polyhedra are called coordination polyhedra because they tell with how many oxygen ions a cation located in a particular polyhedron is coordinated. Naturally, the coordination has a direct bearing on the chemical bond that arises between the cation and its oxygen environment.

In the absolute majority of cases, elements A and B differ in chemical nature (the only exceptions are magnetite or iron-iron spinel, FeFe$_2$O$_4$, and gaussmanite or manganomanganese spinel, MnMn$_2$O$_4$), and in the charge state, which is determined by the oxidation state of the cation.

This prompts the question: How should two kinds of cations differing in chemical nature and charge state be arranged in two polyhedra differing not only in geometry but also, and more importantly, in the bonding energy between the cations and the surrounding oxygen ions? In the literature [2], this difference is referred to as nonequivalent positions.

When cations A are located in tetrahedra and have an oxidation state of $2^+$ and cations B are in octahedra and have an oxidation state of $3^+$, the spinel is referred to as normal. It contrasts with the inverse arrangement in which the tetrahedra contain cations B, whereas the octahedra contain equal numbers of cations A and cations B. Moreover, cation B at a tetrahedral site retains an oxidation state of $3^+$, and cation A at an octahedral site has an oxidation state of $2^+$. That is, the octahedral oxygen environment has two kinds of cations differing in the charge state.

The inversion may be incomplete, resulting in what is known as a partially inverted spinel.

Fig. 1. Relative position of an anion octahedron and an anion tetrahedron in the spinel structure [1]: ○ oxygen; □ cation in the tetrahedron; ○ cation in the octahedron; α lattice constant.

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Apart from spinels of general formula $A_2B_3^2\text{O}_4$, some other ternary compounds can also have a spinel structure, with component A ordinarily having an oxidation state of $1^+$ and component B an oxidation state of $4^+$, and even some binary compounds.

The above question can be answered from thermodynamic views on the crystal structure.

The unit cell of a spinel has 8 formula units. Therefore, in the case of an ideal lattice, it would contain 32 oxygen sites, 64 tetrahedral sites, and 32 octahedral sites. For an equilibrium spinel structure, however, it is typical that in the ideal lattice only the oxygen sites will be fully occupied, whereas not more than one-eighth of the tetrahedral sites and not more than half the octahedral sites will be filled. In such a situation, the crystal will have a minimal potential energy and a maximal stability. This is the equilibrium, thermodynamically stable state for the crystal. Any departure from such a state would need a certain energy input and should be accompanied by an increase in the energy stored in the crystal and by a decrease in its stability.

Hence, if we assume, subject to the above condition, that the spinel has an equal chance to exist in both forms and that the internal energy of each is $E_{\text{int}} = \min$, then we will have to look for the factors necessary for this condition to be satisfied because the two forms are substantially different.

At this writing, two mutually complementary approaches to the problem have taken a well-defined shape. One draws upon theory and invokes quantum-mechanical principles in calculation. The other relies upon thermodynamics and has at its foundation either direct experiments or calculations using the fundamental thermodynamic characteristics of substances obtained experimentally and tabulated in reference books.

The principles and techniques of quantum-mechanical calculations are given fairly full coverage in monographs by Blassee [3], Kreger [4], and Krupicka [5]. The authors make on the following assumptions. Inside a polyhedron, a cation is acted upon by the electrical field set up by the oxygen ions that make up the polyhedron. Because of this, the electron levels of the cation are split, and its energy is now lower than it was prior to the level splitting. The difference between the two have come to be called the stabilization energy. It is a function of both the electronic configuration of the ion involved, and the field energy determined by the structure of the polyhedron. This field stabilizes a cation in a polyhedron. Therefore, energy of the same kind of cation but in different polyhedra must in principle be likewise different. This difference, known as the preferred energy, indicates which of two unlike polyhedra (or nonequivalent positions) a given cation would prefer to populate when the spinel is in a state of equilibrium.

It is customary to determine (calculate) the preferred energy of cations for octahedral sites. It is the difference between the stabilization energies of cations at tetrahedral and octahedral sites. If it is negative, this implies that, with a cation occupying an octahedral site, the internal energy of the system will decrease and, consequently, the system will become more stable compared to what would have been the case if the cation occupied a tetrahedral site. If calculations yield a positive preferred energy for the octahedral oxygen environment, this implies that an octahedral site is denied to the cation because otherwise the system would have stored up more energy instead of releasing it.

When, as usual, a spinel is formed of two kinds of cations differing in nature, the site distribution which assures that the system will have minimal internal energy depends on the difference between the stabilization energies of each cation at a tetrahedral and an octahedral site. A cation with a higher energy in absolute value (with a greater reduction in energy) will occupy an octahedral site, and a cation with lower energy will occupy a tetrahedral site.

What one actually needs to ascertain all of this is solely to know the stabilization energy of a given cation in a given polyhedron. It is calculated by the theory of the electrical field that is created in the oxygen polyhedron, with allowance for the quantum characteristics of the cation's electronic configuration.

The thermodynamic approach to the problem is analyzed in detail by Reznitskii [2, 6, 7]. With it, one need not know the stabilization energies of cations in the respective polyhedra, and if one uses such knowledge, one does so solely to compare experimental and calculated preferred energies.

It is very simple to determine the preferred energies when one of the oxides, a potential component of the spinel, can exist in two crystal chemical modifications typical of the spinel; that is, when the cation has a tetrahedral coordination in one and an octahedral coordination in the other. If the heats of formation for these modifications are known, then the difference between them will represent the preferred energy of the cation for a particular coordination. If the heats of formation are not known, the desired result can be obtained by a calorimetric experiment in which the transition from one modification to the other is accompanied by a thermal effect. Lastly, it is possible to measure the thermal effect when the oxide that contains a cation four-coordinated with oxygen is dissolved in an oxide that contains a cation of different chemical nature but with an octahedral coordination.

There are several more ways in which the problem can be tackled thermodynamically (calorimetrically). In particular, special promise is held by the approach successfully pursued by Urusov [8]. Using models of regular solutions (whose components are cations in nonequivalent positions) and calorimetric data, he has calculated the preferred energies with respect to octahedral sites for some cations. His results closely agree with those obtained by other thermodynamic methods [7].

If one ranks the preferred energies for an octahedral oxygen environment, found as described above, in increasing order for all cations making up the spinels, a pattern can be deduced from which one can predict a priori how particular cations would be distributed among the sites in a particular spinel. More specifically, of any two cations from the series,