

## On the Conditions Pertaining to the Applicability of Végard's Rule in Spinel Solid Solution

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Received May 11, 1982; in revised form November 19, 1982

Within the elastic atomic interaction approximation, conditions which are specified under Végard's rule for the concentration dependence of the multisublattice solid solution lattice parameter is satisfied. The problem was studied by considering the example of two sublattice solid solutions with a spinel structure. The proposed theory and experimental factors are in good agreement.

### Introduction

Existing static-thermodynamic solid solution theories as a rule employ phenomenological values for the energy mixing term. The connection of such values with crystal chemical characteristics of atoms is not clear. In most approximations (Bragg-Williams, quasichemical, and others), the energy change solid solution caused by various types of elastic effects is ignored. That is why the thermodynamic calculation of structural parameters of substances is quite unsatisfactory.

In the present paper a calculation of multisublattice solid solution lattice distortions is provided using an elastic model (1-6). The results of the calculations are used to study deviation from the empirical Végard rule which specifies a linear concentration dependence of the crystal lattice parameter. The recognition of the conditions under which this rule is satisfied is especially important for controlling the compositions of compounds. The problem was studied by considering the example of two sublattice solid solutions with a spinel

structure. However, the author believes that such restriction does not influence the essence of the conclusions, the latter being general in character. The exact quantitative conditions under which Végard's rule is fulfilled (within the proposed approximation), and the conditions for deviation from it for solid solutions with some other crystal structures can be obtained provided the structural features of the lattice geometry in the quasielastic crystal energy equation are included.

### Quasielastic Model of Cation-Anion Bonds

We will consider a solid solution with a spinel structure. Let the isomorphic substitution of atoms take place in the octahedral sublattice  $A[B_{2(1-c)}B'_{2c}]O_4$  (square brackets designate the atoms in octahedral positions). Suppose  $c \ll 1$ : in the solid solution there are  $2N_{B'}$  impurity ions  $B'$ ,  $N$  atoms of type  $A$ , and  $2(N - N_{B'})$  atoms of type  $B$ . The exact position of the anion in a spinel structure is determined by the anion parameter. Upon substituting one of the atoms in

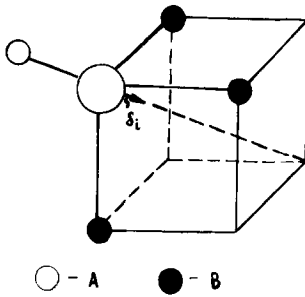


FIG. 1. Oxygen ion displacement in the spinel structure.

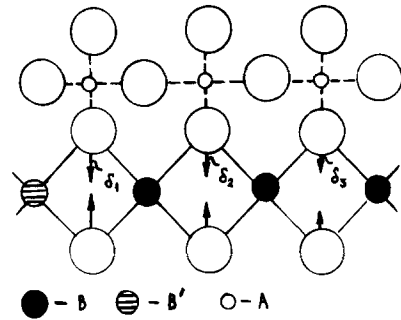


FIG. 2. Oxygen ion displacement for the cation substitution in *B* sublattice of a spinel.

the lattice, the anion displacement along a special body diagonal in the [111] direction takes place, thus resulting in a change in the anion parameter. Let  $\delta_i$  ( $i = 1, 2, \dots, 2m - 2$ ) be the value of the anionic displacement from its position in the lattice. We believe that the  $m$ th anion will remain in its position, being on the boundary of perturbation region. Any anion displacement in a

distorted chain (Figs. 1, 2) leads to the interion distance change ( $\delta$ ). Thus, e.g., the octahedral "cation-anion" distance reduction by  $\delta_i$  is connected simultaneously, with a corresponding tetrahedral increase by  $\sqrt{3} \delta_i$ . When allowing for all these lattice geometry characteristic features, the elastic crystal energy can be written

$$E = [N - (2m - 1)N_{B'}] \left[ k_A^t \left( \frac{a\sqrt{3}}{8} + \bar{X} - l_A \right)^2 + 2k_B^o \left( \frac{a}{4} - \frac{\sqrt{3}}{3} \bar{X} - l_B^o \right)^2 \right] + 2N_{B'} \left\{ K_B^o \left( \frac{a}{4} - \frac{\sqrt{3}}{3} \bar{X} - l_B^o + \delta_1 \right)^2 + k_B^o \left( \frac{a}{4} - \frac{\sqrt{3}}{3} \bar{X} - l_B^o - \delta_1 + \delta_2 \right)^2 + \dots + k_B^o \left( \frac{a}{4} - \frac{\sqrt{3}}{3} \bar{X} - l_B^o + \delta_{2m-1} - \delta_{2(m-1)} \right)^2 + \frac{1}{2} k_A^t \left[ \left( \frac{a\sqrt{3}}{8} + \bar{X} - l_A - \sqrt{3}\delta_1 \right)^2 + \left( \frac{a\sqrt{3}}{8} + \bar{X} - l_A + \sqrt{3}\delta_1 - \sqrt{3}\delta_2 \right)^2 \dots + \left( \frac{a\sqrt{3}}{8} + \bar{X} - l_A + \sqrt{3}\delta_{2(m-1)} - \sqrt{3}\delta_{2m-1} \right)^2 \right] \right\}$$

where  $a$  is the cubic elementary cell parameter,  $k_{A,B,B'}^t$  is the "rigidity" of the  $A, B, B'$  cation bonds with the anion in tetrahedral (t) and octahedral positions (o),  $l_{A,B,B'}^o$  are the corresponding distances of unstrained bonds, and  $\bar{X}$  for a normal spinel is defined by (5)

$$\bar{X} = \frac{2\sqrt{3}k_B^o \left( \frac{a}{4} - l_B^o \right) - 3k_A^t \left( \frac{a\sqrt{3}}{8} - l_A \right)}{3k_A^t + 2k_B^o}$$

After some transformations the quasielastic energy of solid solution cation-anion bonds related to one formula unit is

$$E = E_0 + 2c \left\{ k_B^o \left[ \frac{k_B^o}{k_B^o} \left( \frac{a}{4} - \frac{\sqrt{3}}{3} \bar{X} - l_B^o + \delta_1 \right)^2 - \left( \frac{a}{4} - \frac{\sqrt{3}}{3} \bar{X} - l_B^o \right) \left( \frac{a}{4} - \frac{\sqrt{3}}{3} \bar{X} - l_B^o + 2\delta_1 \right) + \sum_{i=1}^{2(m-1)} (\delta_{i+1} - \delta_i)^2 \right] + \frac{3}{2} k_A^t \left[ \delta_1^2 + \sum_{i=1}^{2(m-1)} (\delta_i - \delta_{i+1})^2 \right] \right\}. \quad (1)$$

In (1)

$$c \equiv \frac{N_{B'}}{N_B}, \quad E_0 \equiv k_A^1 \left( \frac{a\sqrt{3}}{8} + \bar{X} - l_A^1 \right)^2 + 2k_B^0 \left( \frac{a}{4} - \frac{\sqrt{3}}{3}\bar{X} - l_B^0 \right)^2.$$

Solving the equation system  $\partial E/\partial \delta_i = 0$  ( $i = 1, 2, 3, \dots, 2m-2$ ) we define the local displacement from parametric positions as

$$\delta_i = \frac{[2m - (i + 1)] \left[ \left( \frac{a}{4} - \frac{\sqrt{3}}{3}\bar{X} \right) (k_B^0 - k_{B'}^0) + k_{B'}^0 l_{B'}^0 - k_B^0 l_B^0 \right]}{4(m-1)(k_{B'}^0 + k_B^0 + 3k_A^1) - (2m-3)(2k_B^0 + 3k_A^1)}.$$

Substituting  $\delta_i$  at  $m \rightarrow \infty$  in (1) we have

$$E = E_0 + (2k_{B'}^0 + 3k_A^1)^{-1} \left\{ (k_{B'}^0 - k_B^0)(2k_B^0 + 3k_A^1) \left( \frac{a}{4} - \frac{\sqrt{3}}{3}\bar{X} \right)^2 - 2(2k_B^0 + 3k_A^1)(k_{B'}^0 l_{B'}^0 - k_B^0 l_B^0) \right. \\ \left. - k_{B'}^0 l_{B'}^0 \left( \frac{a}{4} - \frac{\sqrt{3}}{3}\bar{X} \right) + 2k_{B'}^0 l_{B'}^0 (2k_{B'}^0 l_{B'}^0 - k_{B'}^0 l_{B'}^0 - k_B^0 l_B^0) + 3k_A^1 (k_{B'}^0 l_{B'}^0 - k_B^0 l_B^0) \right\} C. \quad (2)$$

Making an analogous calculation, we find that for substitution in the *A* sublattice the concentration term in the quasielastic energy equation can be written

$$[2(2k_B^0 + 3k_A^1)]^{-1} \left\{ (k_A^1 - k_A^0)(2k_B^0 + 3k_A^1) \left( \frac{a\sqrt{3}}{8} + \bar{X} \right)^2 - 2(2k_B^0 + 3k_A^1)(k_A^1 l_A^1 - k_A^0 l_A^0) \right. \\ \left. - k_A^1 l_A^1 \left( \frac{a\sqrt{3}}{8} + \bar{X} \right) + 3k_A^1 l_A^1 (2k_A^1 l_A^1 - k_A^1 l_A^1 - k_A^0 l_A^0) + 2k_B^0 (k_A^1 l_A^1 - k_A^0 l_A^0) \right\}. \quad (3)$$

When an atomic displacement occurs simultaneously in both solid solution sublattices, it becomes necessary to add component (3) to Eq. (2) (for small concentrations the chain distortion regions caused by displacements in the *A* and *B* sublattices are considered independent). The equilibrium lattice parameter value is determined from the condition  $\partial E/\partial a = 0$ . To within a linear concentration term for *A* displacements,  $a(c)$  takes on the form

$$a = a_0 - \frac{8\sqrt{3}k_A^1(2k_B^0 + 3k_A^1)(l_A^1 - l_A^0)}{3k_A^1(2k_B^0 + 3k_A^1)} C. \quad (4)$$

For *B* displacements the concentration lattice parameter dependence assumes the form

$$a = a_0 - \frac{8k_B^0(3k_A^1 + 2k_B^0)(l_B^0 - l_{B'}^0)}{3k_B^0(2k_B^0 + 3k_A^1)} C. \quad (5)$$

In Eqs. (4) and (5)

$$a_0 \equiv \frac{8}{9}(l_B^0 + \sqrt{3}l_A^0).$$

## Results and Discussion

Let us define the deviation of  $a(c)$  from the straight line, corresponding to Végard's rule for solid solutions  $A_{1-c}A'_cB_{2(1-c)}B'_{2c}O_4$  for  $c \rightarrow 0$  and  $c \rightarrow 1$ :

$$\Delta_1 = \frac{da}{dc} \Big|_{c=0} - \tan \alpha$$

$$\Delta_2 = \tan \alpha - \frac{da}{dc} \Big|_{c=1}, \quad (6)$$

where  $\tan \alpha = \frac{8}{9}(l_{B'}^0 - l_B^0) + 8\sqrt{3}/9(l_A^1 - l_A^0)$ . Then  $\Delta_1$  is found to be

$$\Delta_1 = \Delta_t + \Delta_0 = \frac{16\sqrt{3}k_B^0(k_A^t - k_A^i)(l_{A'}^t - l_A^i)}{9k_A^t(2k_B^0 + 3k_A^t)} - \frac{8k_A^t(k_B^0 - k_{B'}^0)(l_{B'}^0 - l_B^0)}{k_B^0(2k_{B'}^0 + 3k_A^t)}. \quad (7)$$

The equation for  $\Delta_2$  has an analogous form. The analysis of the equations for  $\Delta_1$  and  $\Delta_2$  allows one to establish some characteristic features of the concentration parameter dependence of the solid solution lattice in a multisublattice crystal.

(1) If cation displacements occur only in the *A* sublattice or only in the *B* sublattice, the Végard rule is satisfied when one of two independent conditions is used:

$$(a) \quad k_{A,B}^{t,0} \approx k_{A',B'}^{t,0} \quad (b) \quad l_{A,B}^{t,0} \approx l_{A',B'}^{t,0}.$$

Supposing, as in earlier work (4–6), that bond rigidity is directly proportional to the formal cation charge and inversely proportional to its coordination number, condition (a) can be written as  $z_{A,B} = z_{A',B'}$ . Thus, for isovalent displacements in one of the sublattices, the concentration dependence of the crystal lattice parameter always satisfies Végard's rule. The bond distance can be represented as the summation of cation and anion radii. Hence, the sufficiency condition (b) can be specified as follows: Végard's rule holds if the radii of the substituting and substituted cations are equal:  $r_{A,B}^{t,0} \approx r_{A',B'}^{t,0}$ . The available experimental information on oxygen and chalcogenide spinels is in good agreement with our results. In accordance with condition (a) in solid solutions  $\text{ZnAl}_{2(1-c)}\text{Cr}_{2c}\text{S}_4$  and  $\text{ZnAl}_{2(1-c)}\text{Cr}_{2c}\text{O}_4$  Végard's rule is fulfilled (7). The following fact is also of interest: In the  $\text{ZnAl}_{2(1-c)}\text{Cr}_{2c}\text{S}_4$  system, on substitution of  $\text{Cr}^{3+}$  for  $\text{Al}^{3+}$  a linear decrease of lattice period is observed, while in  $\text{ZnAl}_{2(1-c)}\text{Cr}_{2c}\text{S}_4$  a linear increase is observed. Apparently there is a substantial difference in the nature of the cation–anion chemical bond in oxygen as opposed to sul-

fide spinels, which is expressed in the fact that  $l_{\text{Cr-O}}^0 > l_{\text{Al-O}}^0$ , while  $l_{\text{Cr-S}}^0 < l_{\text{Al-S}}^0$  (4, 5). It is worth noting that in an isovalent displacement the deviation of  $a(c)$  from a straight line, corresponding to Végard's rule, may be associated either with a change in the cation valency state ( $\text{Co}_{1-c}\text{Cu}_c\text{Cr}_2\text{S}_4$  (8),  $\text{CuCr}_{2(1-c)}\text{V}_{2c}\text{S}_4$  (9, 10)) or with ordering of ions in the tetrahedral or octahedral sublattice of a solid solution (e.g., in the  $\text{CoRh}_{2(1-c)}\text{Co}_{2c}\text{S}_4$  system a positive deviation from Végard's rule, connected with ions ordering in the *B* sublattice (8) is observed).

The conditions under which (a) and (b) fulfill Végard's rule are also confirmed by experimental data for multisublattice solid solutions with perovskite (3), garnet (11, 12), and other structures.

(2) When cation displacements occur simultaneously both in *A* and *B* sublattices, Végard's rule applies in two cases. First, when either of the (a) or (b) conditions is satisfied. Secondly, when the elastic bond distances and bond rigidity are such that  $\Delta_1 = 0$  at  $k_{A,B}^{t,0} \neq k_{A',B'}^{t,0}$  and  $l_{A,B}^{t,0} \neq l_{A',B'}^{t,0}$ , i.e., under the condition

$$2\sqrt{3}k_B^0(2k_{B'}^0 + 3k_A^t)(k_A^t - k_{A'}^t)(l_{A'}^t - l_A^t) \approx 9k_A^t(2k_B^0 + 3k_{A'}^t)(k_B^0 - k_{B'}^0)(l_{B'}^0 - l_B^0). \quad (8)$$

(3) Analyzing empirical data, Verwey stated that in solid solutions made with components with a similar degree of inversion the crystal lattice parameter changes linearly as a function of composition. Deviations from linear dependence are observed when normal spinels are dissolved with inverted ones (Verwey's rule (13, 14)). In this case the  $a(c)$  nonlinearity is due to cation redistribution along nonequivalent crystallographical lattice positions. This hypothesis is substantiated by the cluster component model (15). It is of interest that the deviation from the  $a(c)$  linear dependence, as the equation analysis for  $\Delta_1$  and  $\Delta_2$  shows, is possible even when cation re-

distribution along nonequivalent positions does not occur. Thus, for  $a(c)$  to become convex, it is necessary that  $\Delta_1 > 0$ ,  $\Delta_2 > 0$ , while for  $a(c)$  to be concave, it is necessary that  $\Delta_1 < 0$  and  $\Delta_3 < 0$ . These conditions become suitable for a calculation criterion, if in Eq. (8) the equality sign is replaced by an inequality. The result obtained supplements the Verwey rule and needs to be checked experimentally (Fig. 3).

Equations (4)–(7) permit one also to explain quantitatively the complex character of the  $a(c)$  dependence for some "normal-

inverse spinel" solid solutions. We consider the  $\text{FeCr}_{2(1-c)}\text{Fe}_{2c}\text{O}_4$  system. Proceeding from the crystal field stabilization energy (16, 17), we suppose that with the increase of solid solution concentration  $\text{Cr}^{3+}$  ions will be substituted for  $\text{Fe}^{2+}$  ions in octahedral positions, while  $\text{Fe}^{3+}$  ions (independent of coordination) will be displaced into tetrahedral positions. Moreover, the degree of inversion of the solid solution should increase, while the crystal lattice parameter should decrease. Experimental data (18) contradict such a conclusion. The

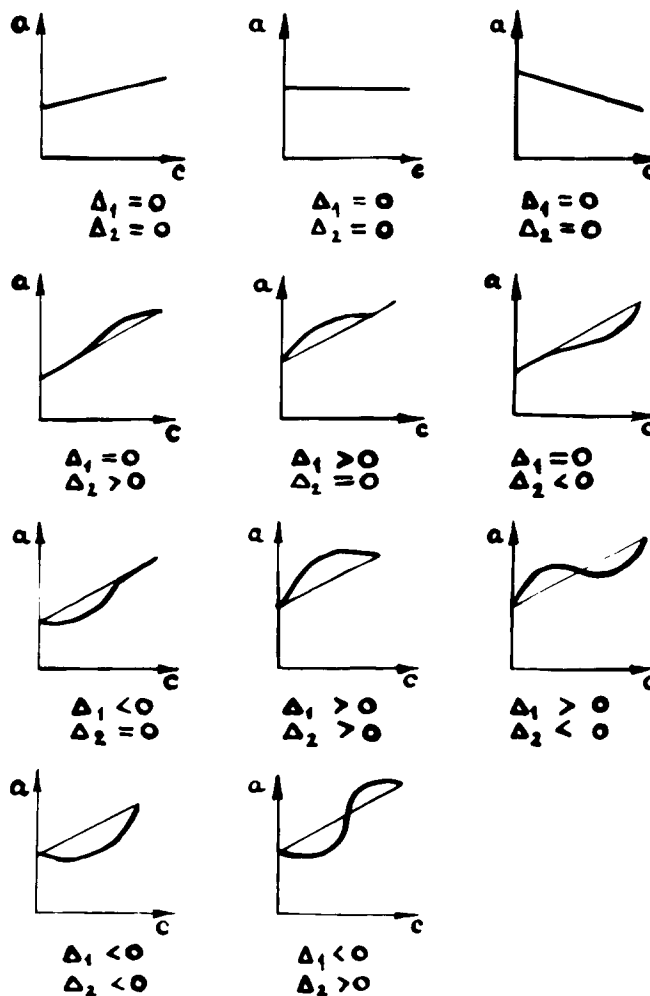


FIG. 3. Possible types of concentration dependence of  $a(c)$  crystal lattice parameter of spinels.

TABLE I  
SOLID SOLUTIONS FOR WHICH VÉGARD'S RULE APPLIES

Solid solutions	Homogeneity regions	References	Solid solutions	Homogeneity regions	References
$\text{Cd}_{1-c}\text{Zn}_c\text{Cr}_2\text{S}_4$	$0 \leq c \leq 1$	(8)	$\text{ZnFe}_{2(1-c)}\text{Rh}_{2c}\text{O}_4$	$0 \leq c \leq 1$	(22)
$\text{Cd}_{1-c}\text{Hg}_c\text{Cr}_2\text{S}_4$	$0 \leq c \leq 1$	(8)	$\text{Ni}_2\text{Si}_c\text{Ge}_{1-c}\text{O}_4$	$0 \leq c \leq 1$	(23)
$\text{Cd}_{1-c}\text{Fe}_c\text{Cr}_2\text{S}_4$	$0 \leq c \leq 1$	(8)	$\text{MnSc}_{2c}\text{Fe}_{2(1-c)}\text{O}_4$	$0 \leq c \leq 1.9$	(24)
$\text{Cu}_{1-c}\text{Ni}_c\text{Cr}_2\text{S}_4$	$0 \leq c \leq 0.74$	(8)	$\text{MgSc}_{2c}\text{Fe}_{2(1-c)}\text{O}_4$	$0 \leq c \leq 1.72$	(24)
$\text{Zn}_{1-c}\text{Cr}_c\text{Al}_2\text{S}_4$	$0 \leq c \leq 1$	(8)	$\text{FeFe}_{2(1-c)}\text{Sc}_{2c}\text{O}_4$	$0 \leq c \leq 0.4$	(24)
$\text{Co}_{1-c}\text{Ni}_c\text{Cr}_2\text{S}_4$	$0 \leq c \leq 0.2$	(8)	$\text{MgCr}_{2(1-c)}\text{Sc}_{2c}\text{O}_4$	$0 \leq c \leq 1.3$	(24)
$\text{Fe}_c\text{Cu}_{1-c}\text{Cr}_2\text{S}_4$	$0 \leq c \leq 0.6$	(21)	$\text{NiFe}_{2(1-c)}\text{Sc}_{2c}\text{O}_4$	$0 \leq c \leq 1.5$	(24)

calculations show that  $\Delta_0 > 0$ , if  $\text{Cr}^{3+}$  ions are substituted for  $\text{Fe}^{3+}$  ions in octahedral positions (when  $c \rightarrow 0$ ). When  $c \rightarrow 1$   $\text{Fe}^{3+}$  ions must be substituted for  $\text{Cr}^{3+}$  ions in octahedral positions and  $\text{Fe}^{2+}$  ions for  $\text{Fe}^{3+}$  ions in tetrahedral positions,  $\Delta_{20} > 0$ ,  $\Delta_{21} < 0$ ,  $\Delta_2 < 0$ . Hence,  $a(c)$  should have a sigmoidal character. Rigidity bonds were calculated using formula 3 from ref. [2]. Furthermore, the calculations showed that the character of  $a(c)$  for solid solutions in which cation displacement occurs only in tetrahedral or only in octahedral positions of the spinel lattice is evidently impossible. It should be noted that a nonlinear  $a(c)$  curve character was found on investigation of heterovalent substitutions in solid solutions with the perovskite structure (19, 20) and in solid solutions with the garnet structure (11). These experimental data speak to the correctness of the theoretical conclusion made.

Table I contains some examples of spinel structure solid solutions with isovalent displacement of cations in one crystallographic site. Végard's law applies to solutions of this type.

The model under consideration can be used only for low concentration at either end of the solid solution, when defect-defect interactions are of no importance. The formulae obtained for  $a(c)$  do not apply to intermediate concentration.

The types of spinel solid solutions considered in this paper are relatively simple. Further development of a quasielastic model appears to require an analysis of more complicated cases, such as "inverted-normal spinel" or "inverted-static spinel" solid solutions. Nevertheless, the results obtained are fairly general in character; they account for a large part of the experimental material, substantiating and confirming some empirical rules in the crystal chemistry of multisublattice solids.

## Conclusions

A consistent theoretical scheme to calculate the distortions occurring in a solid solution crystal lattice with several nonequivalent positions is given. Within the elastic atomic interaction approximation, the exact conditions under which Végard's rule holds are obtained. The calculations are illustrated by an example of a two sublattice spinel structure solution.

## Acknowledgment

The author thanks Professor V. Sakhnenko for helpful discussions of the work.

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