

## The Energetics of Polytypic Structures: a Computer Simulation of Magnesium Silicate Spinelloids

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### Abstract

A computer simulation technique is used to predict the lattice energies, structures and physical properties of magnesium silicate spinelloids from given interatomic potentials. Two types of potential models are considered, a fully ionic model, which includes electrostatic, short-range and dispersive terms, and a partially ionic model, in which fractional charges are allocated to the component ions and a Morse function is included to describe the effect of covalency in the Si–O bond. The calculated energies of the spinelloid polytypes are analysed in terms of the interaction energies between component structural units. The calculated spinelloid energetics are discussed in the light of recently developed models of polytypism. The predicted values of the interaction energy terms are tested by using them to calculate the energy of a  $1/2[101](010)$  stacking fault in the naturally occurring magnesium silicate spinelloid wadsleyite. The calculated stacking-fault energies are in excellent agreement with the value inferred from transmission electron microscopy.

### 1. Introduction

Many crystal structures may be considered to be composed of one or more component structural units or modules. If the relative arrangement of these modules may be varied, the resulting phases are known as polytypes. Polytypism is therefore a special form of polymorphism. There need be no constraint upon the chemistry or structure of the modules involved (Thompson, 1981). However, to be considered polymorphic, the various modes of module stacking should not affect the composition of the phase as a

whole. Polytypism is a common phenomenon, and examples of polytypic materials include the well known SiC, ZnS and mica phases, as well as a wide range of other mineral families such as the spinelloids, pyroxenes and pyroxenoids.

Polytypic series or families characteristically contain a large number of structures, which exhibit a variety of module stacking sequences. Simple shorter-period modifications are most commonly observed, although polytypes may have very-long-period repeats, in some cases in excess of 1000 Å. Because the polytypes of a given compound are composed of virtually identical structural units, the free-energy differences between them are small. As a result, the transformation kinetics between polytypes is often slow, and it is usually difficult to establish thermodynamic equilibrium. Undoubtedly, many metastable phases have been synthesized in such polytypic systems. However, recent careful experimentation upon the SiC and spinelloid systems (Jepps & Page, 1983; Akaogi, Akimoto, Horioka, Takahashi & Horiuchi, 1982) has established that at least some polytypes have thermodynamically definable fields of stability.

A variety of theories have been advanced to explain why some polytypic sequences appear to be more stable or occur more frequently than others (Pandey & Krishna, 1983). Theories based upon growth or kinetic considerations (e.g. Frank, 1951) may well explain how certain metastable sequences are formed; however, thermodynamically based models are required to explain the observed equilibrium phases found in systems such as SiC and the spinelloids. Among the first of such theories was that of Jagodzinski (1954), who argued that long-period polytypes are stabilized by vibrational entropy effects. More recent workers (Hazen & Finger, 1981; Price, 1983*a*; Smith, Yeomans & Heine, 1984; Price & Yeomans, 1984), however, have developed the idea that the relative stability of polytypic structures may be

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determined by considering effective interactions between the component structural units. To explain why long-period polytypic phases are found and to model the nature of the observed phase transformations between polytypes, it is necessary to appeal to interactions between structural units that are effective over a distance greater than that between first-nearest-neighbour modules. In fact, it appears that competing interactions between first and further neighbour units are a pre-requisite for the development of long-period structures (Price & Yeomans, 1984).

Price (1983*a*) analysed the stability of spinelloids and other polytypic structures by considering the effect of interactions between first-, second- and third-nearest-neighbour structural units. He found that phases with periods of up to six modules could be stable at zero temperature. Subsequently, Smith *et al.* (1984) and Price & Yeomans (1984) provided an explanation of the observed equilibrium behaviour of polytypic phases in terms of the axial next-neighbour Ising or ANNNI model. This statistical mechanics model, originally developed to describe magnetic systems (Elliot, 1961; Fisher & Selke, 1981), invokes only first- and second-neighbour interactions, but includes entropic effects (non-zero temperature), in an attempt to describe observed polytypic behaviour. In their use of the ANNNI model, Smith *et al.* (1984) and Price & Yeomans (1984) proposed that the basic polytypic structural unit can be written as a Hamiltonian with competing interactions. The resulting model provides a simple equilibrium description of polytypism, in which short-range couplings can lead to the existence of polytypes with very-long-period stacking sequences. Other important features of polytypism are also explained by this model: notably that only a specific set of polytypes are stable for a given compound, that reversible phase transitions are observed, and that polytypes with short stacking sequences occur most frequently.

The models of Price (1983*a*), Smith *et al.* (1984) and Price & Yeomans (1984) all assume that the internal energy of any given polytypic structure is a function both of the internal energy of the component structural modules and of the energy of interaction between neighbouring modules. These interactions may be due to strain effects resulting from either ion-size mismatch or local electrostatic-charge imbalances at the interfaces between the structural units. They assume that the internal energy of the modules is invariant, and that the difference in the free energies of the polytypic phase is solely dependent upon the interaction energies between structural units and the temperature. Despite the fact that these assumptions are fundamental to their models, neither Price (1983*a*), Smith *et al.* (1984) nor Price & Yeomans (1984) were able to justify them fully or to provide estimates of the magnitude of the interaction-energy terms. To establish the validity of these models, it is

essential that the assumptions upon which they are based should be tested.

The energetics of polytypic phases could be investigated by a number of theoretical and experimental techniques. It would be possible to test the above assumptions by analysing the energetics of a polytypic family inferred from detailed calorimetric studies of the phases involved. Such a study has been performed by Akaogi & Navrotsky (1984) in their investigation of the nickel aluminosilicate spinelloid family. Although their results are excellent, problems would generally be expected with such an experimental approach, since it is virtually impossible to obtain pure unfaulted samples of a specific polytype (*e.g.* Davies & Akaogi, 1983). These structural faults or polytypic intergrowths will influence calorimetric measurements and may well obscure the subtleties of polytype energetics. An alternative approach to direct energy measurements is to use computer modelling techniques to simulate polytypic structures, and use the calculated energies of these simulated phases as a basis for the analysis of polytypic energetics. Recently Catlow (1977), Catlow & Norgett (1978) and Catlow, Cormack & Theobald (1984) have shown that atomistic modelling techniques, based upon energy minimization methods, can be used successfully to predict the structure, and energetic and physical properties of simple ionic compounds. The internal energy and physical properties of the materials are calculated from pair-wise additive interatomic potentials, which include electrostatic, short-range and instantaneous dipole-dipole interaction terms. This approach has been extended by Catlow, Thomas, Parker & Jefferson (1982), Parker (1983), Parker, Catlow & Cormack (1984), Price & Parker (1984) and Matsui & Busing (1984) to the study of silicates and other phases with more complex bonding.

In this paper we will expand upon the work of Price & Parker (1984), and will present an analysis of the energetics of spinelloid polytypes that will enable the assumptions made by previous workers about the systematic energetics of these phases to be tested. Specifically, we will consider the  $\text{Mg}_2\text{SiO}_4$  spinelloid family, both because spinelloids in general exhibit an interesting and well characterized range of polytypic structures, and because the magnesium silicate system is particularly important geologically, as it includes the two minerals ringwoodite and wadsleyite, which make up the majority of the transition zone of the Earth's mantle. In § 2 we describe the structural characteristics of spinelloid polytypes and develop a notation for their description. An outline of the computational techniques and potential models used in this study is provided in § 3, while in § 4 the results of the calculations are presented. These results are discussed, in the light of the models of Price (1983*a*), Smith *et al.* (1984) and Price & Yeomans (1984), in § 5.

## 2. Spinelloid structures

The structural features of spinelloids have been described in a series of papers by Ma & Sahl (1975), Horioka, Takahashi, Morimoto, Horiuchi, Akaogi & Akimoto (1981), Horioka, Nishiguchi, Morimoto, Horiuchi, Akaogi & Akimoto (1981), Horiuchi, Akaogi & Sawamoto (1982) and Akaogi *et al.* (1982). The family takes its name from its most commonly occurring member, the spinel structure, from which the other structures in the family can be derived. Like spinel, spinelloids generally have an  $AB_2O_4$  stoichiometry, and have structures that are based upon a nearly cubic close-packed arrangement of oxygen ions, within which cations occupy both tetrahedrally and octahedrally coordinated sites. Hyde, White, O'Keeffe & Johnson (1982) and Horiuchi *et al.* (1982) point out that the cations define a 'basic structural unit' within the oxygen framework (Fig. 1a) from which all spinelloids can be constructed. The arrangement of the basic structural units is invariant in two orthogonal directions, and generates an infinite sheet, part of which is shown in Fig. 1(b). Variations in the packing of this sheet in the third dimension give rise to the observed range of spinelloid structures. In the spinel structure, the component spinelloid sheets are packed parallel to (110). Adjacent sheets are related by a glide operator of the type  $1/4[112](110)$ , which when regularly repeated generates the spinel structure shown in Fig. 1(c). In the idealized spinel structure (having oxygens in perfect cubic eutaxy)  $1/4[1\bar{1}2]$  is an anion-anion vector, so that the anion arrangement is unchanged by its operation. However, half of the octahedrally coordinated cations and all of the tetrahedrally coordinated

cations are translated to normally empty sites by this vector and thus interfaces between successive glide-related spinelloid sheets can be considered to be antiphase boundaries (Hyde *et al.*, 1982). Consequently, if the basic structural unit shown in Fig. 1(a) is represented by the arrow illustrated, the stacking sequence along [110] of spinel can be described by the code  $\dots\downarrow\uparrow\downarrow\uparrow\dots$  (Horiuchi *et al.*, 1982). In addition to the glide operator, Price, Putnis & Smith (1982), Hyde *et al.* (1982) and Horiuchi *et al.* (1982) noted that successive idealized spinelloid sheets may also be related by a mirror or twin operator. Thus, for example in the idealized  $\beta$ -phase polymorph of  $Mg_2SiO_4$  wadsleyite (Fig. 1d), basic spinelloid structural units are alternately related by mirror and glide operators, and can be represented by the stacking code  $\dots\uparrow\uparrow\downarrow\downarrow\dots$ .

There are naturally an infinite number of stacking sequences that can be generated by combining mirror and glide operators. Several notations have been developed to describe these sequences (*e.g.* Hyde *et al.*, 1982; Price, 1983a), but we will use the one introduced by Fisher & Selke (1981) to describe any given repeating sequence of structural units. In a repeating sequence such as this:

$$\dots\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\downarrow\dots, \quad (1)$$

consecutive mirror-related units, symbolized by sequences of parallel arrows, will be termed bands. The repeating sequence in (1) comprises three bands of two arrows (or 2-bands) followed by one 3-band. This sequence will be denoted  $\langle 2223 \rangle$  or  $\langle 2^33 \rangle$ . Thus, the spinel sequence,  $\dots\uparrow\downarrow\uparrow\downarrow\dots$ , will be denoted by  $\langle 1 \rangle$ , the wadsleyite sequence by  $\langle 2 \rangle$ , and more generally  $\langle n_1 n_2 \dots n_m \rangle$  will refer to a structure where the repeating sequence is made up of  $m$  bands of length  $n_1, n_2, \dots, n_m$ . This notation is similar to the Zhdanov notation used in the description of many polytypic materials.

Important structural differences exist between spinelloid units that are related by a mirror operation and those that are related by a glide operation. The mirror operator generates corner-linked cation coordination tetrahedra, but the glide operator results in the formation of isolated tetrahedral groups. Thus in the  $Mg_2SiO_4$  spinel polymorph ringwoodite, in which Si is tetrahedrally coordinated and Mg octahedrally coordinated, only isolated  $SiO_4$  units occur, but in wadsleyite  $Si_2O_7$  groups are formed. Generally, bands of length  $n$  will be characterized by the development of corner-sharing chains of Si tetrahedra of the type  $Si_nO_{3n+1}$ . The development of corner-sharing tetrahedra produces changes in the coordination of the oxygen atoms in the spinelloid structure. In ringwoodite, every oxygen is bonded to one Si and three Mg cations; however, in wadsleyite the two oxygens that lie in the plane of the mirror have a different coordination: O(1) being coordinated by five

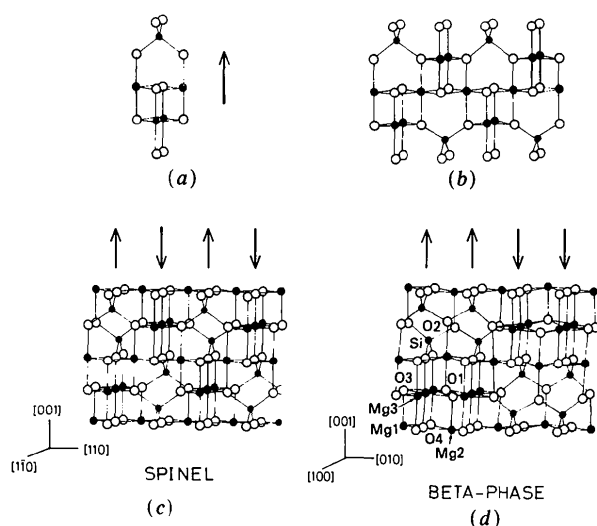


Fig. 1. Perspective views of the spinelloid component units and structures. (a) The 'basic structural unit' (after Horiuchi *et al.*, 1982); (b) the constituent sheet from which all spinelloids can be formed; (c) the spinel structure; (d) the  $\beta$ -phase structure.

Mg cations and O(2) by two Si and one Mg cation (Fig. 1*d*). This configuration produces a partial violation of Pauling's second rule, or the electrostatic valence rule, so that the charge balances on O(1) and O(2) become  $-\frac{1}{3}$  and  $+\frac{1}{3}$  respectively. This charge asymmetry is manifested in structures such as wadsleyite by a local distortion away from oxygen close packing. It is this variation in oxygen coordination, with its resultant structural strains, that makes the two spinelloid stacking operators energetically non-equivalent, and which is implicitly analysed by Price (1983*a*) and Price & Yeomans (1984) when they consider the energy of interaction between first and further neighbour spinelloid units.

It has been noted that neighbouring spinelloid structural units may be orientated in the same sense (represented by the code  $\uparrow\uparrow$  or  $\downarrow\downarrow$ ) or in the opposite sense ( $\uparrow\downarrow$ ) or ( $\downarrow\uparrow$ ). The proportion of *i*th-neighbour pairs of each type within any possible stacking sequence is restricted by the relationship

$$Z_{\uparrow\uparrow,i} + Z_{\downarrow\downarrow,i} + Z_{\uparrow\downarrow,i} + Z_{\downarrow\uparrow,i} = 1, \quad (2)$$

where  $Z_{\uparrow\uparrow,i}$  and  $Z_{\downarrow\downarrow,i}$  are the fraction of *i*th-neighbour layers within the stacking sequence that have the same orientation (mirror related), and  $Z_{\uparrow\downarrow,i}$  and  $Z_{\downarrow\uparrow,i}$  are the proportions of *i*th-neighbour layers that have the opposite orientation (glide related). Thus, for the spinel structure,  $\langle 1 \rangle$ , which has a stacking code  $\dots \uparrow\downarrow\uparrow\downarrow\uparrow\downarrow \dots$ ,  $Z_{\uparrow\uparrow,1} = Z_{\downarrow\downarrow,1} = 0$ ,  $Z_{\uparrow\downarrow,1} = Z_{\downarrow\uparrow,1} = 0.5$ ,  $Z_{\uparrow\uparrow,2} = Z_{\downarrow\downarrow,2} = 0.5$ ,  $Z_{\uparrow\downarrow,2} = Z_{\downarrow\uparrow,2} = 0$ , etc.

Price (1983*a*) argued that the total ground-state energy of any given stacking sequence, per layer in that sequence, can be expressed as

$$E = -\sum_i (Z_{\uparrow\uparrow,i} J_{\uparrow\uparrow,i} + Z_{\downarrow\downarrow,i} J_{\downarrow\downarrow,i} + Z_{\uparrow\downarrow,i} J_{\uparrow\downarrow,i} + Z_{\downarrow\uparrow,i} J_{\downarrow\uparrow,i}) + E_I, \quad (3)$$

where  $J_{\uparrow\uparrow,i}$  and  $J_{\downarrow\downarrow,i}$  are the interaction energies between *i*th-neighbour layers that have the same orientation,  $J_{\uparrow\downarrow,i}$  and  $J_{\downarrow\uparrow,i}$  are the interaction energies between *i*th-neighbour layers orientated in the opposite sense, and  $E_I$  is the internal energy of a spinelloid layer. However, for all polytypic structures of this type  $J_{\uparrow\uparrow,i} = J_{\downarrow\downarrow,i}$  and  $J_{\uparrow\downarrow,i} = J_{\downarrow\uparrow,i}$ , so we can write

$$E = \sum_i (Z_i J_i - J_{\uparrow\uparrow,i}) + E_I \quad (4)$$

$$= \sum_i Z_i J_i + E_{(\infty)}, \quad (5)$$

where  $J_i = J_{\uparrow\uparrow,i} - \frac{1}{2}(J_{\uparrow\downarrow,i} + J_{\downarrow\uparrow,i})$ ,  $Z_i = Z_{\uparrow\downarrow,i} + Z_{\downarrow\uparrow,i}$ , and  $E_{(\infty)}$  is the lattice energy of the  $\langle \infty \rangle$  structure. This formulation is analogous to that used by Price & Yeomans (1984) in which the ground-state energy per spinelloid unit was written as

$$E = -\frac{1}{2} N \sum_i \sum_j L_j L_{j+1} + E_I, \quad (6)$$

where  $N$  is the number of layers in the repeating

sequence, and  $L_i = +1$  or  $-1$  if a given layer is in a state  $\uparrow$  or  $\downarrow$  respectively. In this case

$$Z_i = \frac{1}{2} \left[ 1 - \sum_j L_j L_{j+1} / N \right] \quad (7)$$

and

$$E_{(\infty)} = E_I - \frac{1}{2} \sum_i J_i. \quad (8)$$

In the following sections, we will attempt to quantify the energies of interaction ( $J_i$ ) between spinelloid units, by using interatomic potentials designed to reproduce their structural characteristics and the lattice energies of a variety of spinelloid polytypes.

### 3. Potential models

We have developed two sets of interatomic potentials to describe spinelloid structures, one of which is a fully ionic potential and the other a partially ionic model. The fully ionic potential used in this study is represented by the expression

$$V_{ij}(r) = q_i q_j r^{-1} + f(B_i + B_j) \times \exp [(A_i + A_j - r)/(B_i + B_j)] - C_{ij} r^{-6}, \quad (9)$$

where  $q_i$  and  $q_j$  are the formal point charges associated with atoms  $i$  and  $j$ ,  $r$  is the interatomic distance,  $A_{i,j}$  and  $B_{i,j}$  (with units of length) are empirically derived terms related to the relative sizes and compressibilities of the atomic species,  $f$  is a constant with dimensions of energy per unit length, and  $C_{ij}$  is a term to describe the attractive instantaneous dipole-dipole interactions between  $i$  and  $j$ .

It is well established that bonding in silicates is not fully ionic (*e.g.* Pauling, 1960). Consequently, in addition to using a fully ionic model in which  $q_i$  and  $q_j$  are integral numbers, we model the energetics of the magnesium silicate spinelloids using a partially ionic potential in which the  $q_i$  terms are allowed to be non-integral (Price & Parker, 1984). In this model the effect of covalent bonding between Si and O atoms is described explicitly by the addition of a Morse term to the potential, with the form

$$V_{ij}(r) = D_{ij} \{ \exp [-2E_{ij}(r - r^*)] - 2 \exp [-E_{ij}(r - r^*)] \}, \quad (10)$$

in which  $r^*$  is the equilibrium Si-O bond length (taken as 1.63 Å),  $D_{ij}$  is the empirically determined Si-O covalent-bond strength, and  $E_{ij}$  is a constant determined by the vibrational behaviour of the Si-O bond, which was calculated to be 1.975 Å<sup>-1</sup> from the vibrational spectrum of the Si-O diatomic molecule (Herzberg, 1950).

Price & Parker (1984) used the programs *WMIN* (Busing, 1981) and *METAPPCS* (Catlow *et al.*, 1984)

Table 1. *Potential parameters*

[The terms  $A_i$  in potential  $P1$  are corrected values and not those misquoted in Price & Parker (1984).]

|  | Charge | $A_i$<br>(Å) | $B_i$<br>(Å) | $C_{O-O}$<br>(kJ mol <sup>-1</sup> Å <sup>6</sup> ) | $D_{Si-O}$<br>(kJ mol <sup>-1</sup> ) |
|--|--------|--------------|--------------|---|---------------------------------------|
| <b>Terms in <math>P1</math></b>        |        |              |              |   |                                       |
| O                                      | -2.0   | 1.1228       | 0.0745       | 5796.6  |                                       |
| Mg                                     | +2.0   | 2.3003       | 0.2200       |   |                                       |
| Si                                     | +4.0   | 3.1057       | 0.3412       |   |                                       |
| <b>Extra term in <math>P1a</math></b>  |        |              |              |   |                                       |
| O(1)                                   | -2.0   | 1.1228       | 0.0745       | 2690.0  |                                       |
| <b>Terms in <math>P4</math></b>        |        |              |              |   |                                       |
| O                                      | -1.208 | 1.4745       | 0.0568       |   | 430.8                                 |
| Mg                                     | +1.726 | 1.6297       | 0.1969       |   |                                       |
| Si                                     | +1.380 | 1.0763       | 0.1706       |   |                                       |
| <b>Extra terms in <math>P4a</math></b> |        |              |              |   |                                       |
| O(1)                                   | -1.665 | 1.6060       | 0.0833       |   |                                       |
| O(2)                                   | -0.740 | 1.4858       | 0.0655       |   | 250.8                                 |
| Mg(2)                                  | +1.715 | 1.5397       | 0.1731       |   |                                       |

to determine the optimum values of the variable terms in a number of potentials developed to describe interatomic forces in magnesium orthosilicates. These programs vary the potential coefficients until the sum of the squares of the first derivatives of the lattice energy with respect to the atomic coordinates and lattice parameters is minimized. In a second mode, the programs can use a set of coefficients for a potential to predict the corresponding minimum-energy structure. This structural minimization can be carried out under totally unconstrained conditions (equivalent to a state of zero confining pressure), or under conditions equivalent to the effect of a given hydrostatic pressure. The program *METAPOCS* can also be used to calculate the dielectric and elastic constants of a perfect lattice from a given potential, using the standard relationships between these constants and the second derivatives of the lattice energy with respect to the atomic coordinates.

By fitting potential parameters to the X-ray-determined structure of forsterite, the olivine structure polymorph of  $Mg_2SiO_4$ , Price & Parker (1984) investigated a range of potential models. They found that partially ionic models were generally the most successful in describing the  $Mg_2SiO_4$  system, being able not only to reproduce the zero-pressure structural and physical properties of forsterite and ringwoodite, but also to model their pressure dependence. The partially ionic model  $P4$  (Table 1) developed by Price & Parker (1984) was the basis for one of the potentials used in this study. This potential possesses fractional ionic charges that compare well with those inferred by Fujino, Sasaki, Takéuchi & Sadanaga (1981) from detailed electron-density studies on forsterite. Potential  $P4$  reproduces the forsterite and ringwoodite cell volumes to within 3 and 0.3% respectively, and the predicted Si-O and Mg-O bond lengths in forsterite have a root-mean-square error, when compared with the observed values, of only 0.004 and 0.025 Å respectively. In addition, this potential predicts the elastic

Table 2. *Observed and calculated structural data for wadsleyite*

|                       | Obs*   | $P1$   | $P1a$  | $P4$   | $P4a$  |
|-----------------------|--------|--------|--------|--------|--------|
| $a$ (Å)               | 5.698  | 5.643  | 5.655  | 5.668  | 5.695  |
| $b$ (Å)               | 11.438 | 11.546 | 11.571 | 11.539 | 11.508 |
| $c$ (Å)               | 8.257  | 8.163  | 8.148  | 8.342  | 8.381  |
| $V$ (Å <sup>3</sup> ) | 537.67 | 529.70 | 533.16 | 545.59 | 549.27 |
| O(1) $z$              | 0.2166 | 0.2049 | 0.2073 | 0.2173 | 0.2109 |
| O(2) $z$              | 0.7164 | 0.6976 | 0.6971 | 0.6956 | 0.7034 |
| O(3) $y$              | 0.9900 | 0.9847 | 0.9847 | 0.9847 | 0.9890 |
| $z$                   | 0.2558 | 0.2667 | 0.2669 | 0.2607 | 0.2564 |
| O(4) $x$              | 0.2615 | 0.2777 | 0.2777 | 0.2582 | 0.2600 |
| $y$                   | 0.1225 | 0.1184 | 0.1182 | 0.1204 | 0.1210 |
| $z$                   | 0.9925 | 0.9831 | 0.9827 | 0.9203 | 0.9931 |
| Mg(2) $z$             | 0.9701 | 0.9620 | 0.9620 | 0.9265 | 0.9598 |
| Mg(3) $y$             | 0.1276 | 0.1285 | 0.1282 | 0.1176 | 0.1290 |
| Si $y$                | 0.1198 | 0.1156 | 0.1157 | 0.1228 | 0.1173 |
| $z$                   | 0.6168 | 0.6148 | 0.6143 | 0.6078 | 0.6134 |
| $\Delta H$ (kJ)       | 6.8    | 20.0   | 3.1    | 75.0   | 4.3    |

\* Structural data from Horiuchi & Sawamoto (1981), thermochemical data from Navrotsky & Akaogi (1984).

Table 3. *Observed and calculated Si-O and Mg-O bond lengths in  $\beta$ - $Mg_2SiO_4$  (in Å)*

|                | Obs   | $P1$  | $P1a$ | $P4$  | $P4a$ |
|----------------|-------|-------|-------|-------|-------|
| Si-O(4) (2)    | 1.632 | 1.488 | 1.485 | 1.649 | 1.633 |
| O(3) (1)       | 1.638 | 1.508 | 1.513 | 1.656 | 1.639 |
| O(2) (1)       | 1.701 | 1.693 | 1.694 | 1.640 | 1.703 |
| $I^*$          |       | 0.121 | 0.121 | 0.040 | 0.001 |
| Mg(1)-O(1) (4) | 2.046 | 2.084 | 2.088 | 2.018 | 2.034 |
| O(3) (2)       | 2.115 | 2.183 | 2.182 | 2.182 | 2.153 |
| Mg(2)-O(1) (1) | 2.035 | 1.982 | 1.992 | 2.426 | 2.104 |
| O(4) (4)       | 2.093 | 2.159 | 2.158 | 2.185 | 2.115 |
| O(2) (1)       | 2.095 | 2.189 | 2.195 | 1.926 | 2.149 |
| Mg(3)-O(1) (2) | 2.016 | 2.024 | 2.026 | 2.102 | 2.018 |
| O(3)           | 2.123 | 2.184 | 2.185 | 2.090 | 2.151 |
| O(4) (2)       | 2.128 | 2.188 | 2.187 | 2.067 | 2.155 |
| $I^*$          |       | 0.057 | 0.058 | 0.118 | 0.030 |

$$* I = \left[ \sum_n (d_{\text{obs}} - d_{\text{calc}})^2 / n \right]^{1/2}$$

constants of forsterite and ringwoodite to within 15 and 20% of the measured values. Also used in this study was the fully ionic potential,  $P1$  (Table 1), developed by Price & Parker (1984). Although Price & Parker found that fully ionic potentials do not model the silicates well (typically giving inaccurate predictions of Si-O bond lengths and predicted elastic constants that are too hard), they found that the potential  $P1$  reproduced the energetics of the magnesium orthosilicates satisfactorily, and that the calculated lattice energies were in good agreement with those inferred from thermochemistry (Parker, 1983).

When  $P1$  was used to calculate the wadsleyite structure, a good agreement between predicted and observed cell volume was obtained (Table 2). The calculated energy difference between ringwoodite and wadsleyite was 20.0 kJ mol<sup>-1</sup> compared with the measured value of 6.8 kJ mol<sup>-1</sup> (Navrotsky & Akaogi, 1984). However, as found in the study of forsterite and ringwoodite, the details of the wadsleyite struc-

ture are not modelled well by the fully ionic potential, with root-mean-square errors in the Si–O and Mg–O bond lengths of 0.121 and 0.057 Å respectively (Table 3). The partially ionic model, *P4*, appears to be only a little better than *P1* when applied to wadsleyite, predicting a cell volume in error by 1.5%, and a predicted energy difference between ringwoodite and wadsleyite of 75.0 kJ mol<sup>-1</sup> (Table 2). Although this model gives smaller root-mean-square errors in the predicted Si–O bond lengths, the predicted shapes of the Mg–O coordination polyhedra are less accurate than those of *P1*, with a root-mean-square error in the Mg–O bond length of 0.118 Å (Table 3).

A more detailed analysis of the failure of the *P4* potential indicates that it models poorly the atoms that lie in the plane of the mirror operator [*viz* O(1), O(2) and Mg(2), Fig. 1*d*]. The reason for this failure is not difficult to understand. The different coordination of O(1) and O(2) means that their bonding and hence the interatomic forces they experience are different from those of O(3) and O(4) (the non-bridging oxygens of the Si<sub>2</sub>O<sub>7</sub> group). As a result, the forces acting on O(1) and O(2) are not described by the terms in the interatomic potential *P4*, which only apply to oxygen atoms coordinated by one Si and three Mg atoms. To overcome this problem, we refined new parameters for atoms O(1), O(2) and Mg(2) by fitting to the X-ray-determined structure of β-Mg<sub>2</sub>SiO<sub>4</sub> (Horiuchi & Sawamoto, 1981), and to the measured energy difference between wadsleyite and ringwoodite (Navrotsky & Akaogi, 1984).

The optimum values for the coefficients in potential *P4a* are given in Table 1. The partial ionic charge determined for Mg(2) is virtually the same as that obtained for Mg in potential *P4*, but the charges on O(1) and O(2) are changed considerably from that of oxygen in *P4*, with  $Z_{O(1)} = -1.665$  and  $Z_{O(2)} = -0.740$ . These charges are reasonable since O(1) is not involved in covalent Si–O bonds, but forms only Mg–O bonds (generally considered to be almost fully ionic), while O(2) is more involved with covalent bonding and would be expected to exhibit a smaller ionic charge. With the increased number of parameters in potential *P4a*, increased accuracy of the structural prediction is to be expected (Table 2), and is indeed reflected by root-mean-square errors in the Si–O and Mg–O bond lengths of 0.001 and 0.030 Å respectively (Table 3). A similar partially ionic potential has recently been developed by Matsui & Busing (1985) to describe β-MgSiO<sub>4</sub>. The accuracy of their potential is comparable to that of *P4a*.

Since this study is concerned specifically with the energetics of the spinelloids, a modified fully ionic model was also developed to obtain a calculated energy difference between the wadsleyite and ringwoodite polymorphs in closer agreement with the observed value. The resulting potential, *P1a* (Table 1), only differs from *P1* by having a value

Table 4. Observed and calculated elastic constants, bulk modulus *K* and shear modulus  $\mu$  for β-MgSiO<sub>4</sub> (in TPa)

|                        | Obs   | <i>P1a</i> | <i>P4a</i> |
|------------------------|-------|------------|------------|
| <i>c</i> <sub>11</sub> | 0.360 | 0.414      | 0.382      |
| <i>c</i> <sub>22</sub> | 0.383 | 0.404      | 0.363      |
| <i>c</i> <sub>33</sub> | 0.273 | 0.291      | 0.302      |
| <i>c</i> <sub>44</sub> | 0.112 | 0.109      | 0.080      |
| <i>c</i> <sub>55</sub> | 0.118 | 0.120      | 0.090      |
| <i>c</i> <sub>66</sub> | 0.098 | 0.093      | 0.108      |
| <i>c</i> <sub>12</sub> | 0.075 | 0.099      | 0.140      |
| <i>c</i> <sub>13</sub> | 0.110 | 0.123      | 0.123      |
| <i>c</i> <sub>23</sub> | 0.105 | 0.129      | 0.127      |
| <i>K</i>               | 0.177 | 0.201      | 0.203      |
| $\mu$                  | 0.115 | 0.115      | 0.100      |

\* Data from Sawamoto *et al.* (1984).

for the O(1)–O(1) van der Waals coefficient of 2690.0 kJ mol<sup>-1</sup> Å<sup>6</sup>. The potential *P1a* predicts a free-energy difference between wadsleyite and ringwoodite of 3.1 kJ mol<sup>-1</sup>, but in all other respects is identical to potential *P1*. In Table 4 the calculated elastic constants of wadsleyite are compared with the recently measured values (Sawamoto, Weidner, Sasaki & Kumazawa, 1984). Both *P4a* and *P1a* reproduce these values well, having root-mean-square errors in their predicted bulk moduli (calculated using the Voigt relationship) of 15 and 14% respectively.

We conclude that, in their separate ways, potentials *P1a* and *P4a* both represent adequate models of the two known Mg<sub>2</sub>SiO<sub>4</sub> spinelloids. We therefore feel that they will produce realistic results when applied to other spinelloid structures, and that they can be used to model the systematics of spinelloid energetics. Therefore, in the next section we use both of these potentials to investigate the energetics of magnesium silicate spinelloids.

#### 4. Spinelloid energetics

The programs *WMIN* and *METAPOCS* were used to calculate the lattice energies of five spinelloid polytypes (Table 5). The optimum minimum-energy structures of these spinelloids were calculated either by starting from an idealized structure or from X-ray-determined data of isostructural nickel aluminosilicate spinelloids. All the calculated cell data for the hypothetical magnesium silicate spinelloids were reasonable, with  $a \approx 5.7$ ,  $b \approx n2.85$  and  $c \approx 8.3$  Å, where  $n$  was the number of spinelloid units in the repeating sequence. The calculated Si–O and Mg–O bond lengths were similarly all comparable with those calculated for ringwoodite and wadsleyite.

As expected, potentials *P4a* and *P1a* both predict that as the number of corner-sharing SiO<sub>4</sub> tetrahedra increases above two the lattice energy decreases. Potential *P4a* predicts that, of the phases investigated, ⟨2⟩ is the most stable spinelloid configuration at 0 K and zero pressure, while potential *P1a* predicts

Table 5. Calculated spinelloid lattice energies (in kJ mol<sup>-1</sup>)

|      | Z <sub>1</sub> | Z <sub>2</sub> | Z <sub>3</sub> | Z <sub>4</sub> | P1a        | P4a      |
|------|----------------|----------------|----------------|----------------|------------|----------|
| (1)  | 1.0            | 0.0            | 1.0            | 0.0            | -19 600.15 | -8687.08 |
| (2)  | $\frac{1}{2}$  | 1.0            | $\frac{1}{2}$  | 0.0            | -19 603.23 | -8691.35 |
| (12) | $\frac{2}{3}$  | $\frac{2}{3}$  | 0.0            | $\frac{2}{3}$  | -19 604.23 | -8690.65 |
| (13) | $\frac{1}{2}$  | $\frac{1}{2}$  | $\frac{1}{2}$  | 0.0            | -19 597.80 | -8672.73 |
| (3)  | $\frac{1}{3}$  | $\frac{1}{3}$  | 1.0            | $\frac{2}{3}$  | -19 587.58 | -8668.27 |

that under these conditions (12) should be more stable than (2) by 1.0 kJ mol<sup>-1</sup>. The (12) magnesium silicate spinelloid has never been reported in nature, although local development of this stacking configuration has been seen in high-resolution electron microscopy studies (Price, 1983*b*). Since all Mg<sub>2</sub>SiO<sub>4</sub> spinelloids are metastable with respect to olivine at zero pressure and temperature it is not possible to check whether the prediction made by P1a is correct.

The values of Z<sub>*i*</sub> (*i* ≤ 4) for the spinelloid structures under consideration were determined by inspection, and are given in Table 5. These values of Z<sub>*i*</sub> and the calculated lattice energies were used to calculate the interaction energies J<sub>*i*</sub> for *i* ≤ 4, which are shown in Table 6. The fact that J<sub>1</sub> and J<sub>2</sub> are calculated to have the largest magnitudes is in accord with the intuitively held belief that longer-range interactions are less significant than those between nearest neighbours. Nevertheless, the calculations indicate that interaction energies are still significant between fourth-nearest neighbours or equivalently over a distance of ≥11 Å. Interestingly, Cormack, Tasker & Catlow (1982) have found that interactions over distances as great as 50 Å play a significant role in determining the relative positions of crystallographic shear planes in non-stoichiometric oxides; therefore the findings for spinelloids need not be surprising.

Both potentials predict that the signs of the first two interaction terms should be negative, but P4a predicts magnitudes for these two terms that are a factor of three or four larger than those predicted by P1a. Potential P4a also predicts that J<sub>3</sub> and J<sub>4</sub> are an order of magnitude smaller than J<sub>1</sub> and J<sub>2</sub>, but values of J<sub>3</sub> and J<sub>4</sub> obtained with P1a are of the same order as those calculated for the nearer-neighbour interactions. The magnitude of J<sub>1</sub> predicted by potential P1a is ~0.1% of the total lattice energy, while P4a predicts it to be ~0.8% of the total energy. To assess the absolute accuracy of our calculations, and to determine whether their relative differences are significant, it is vital to have some way of comparing our results with some other measure of the energetics of interaction between spinelloid units. This can be achieved by using our calculated J<sub>*i*</sub> values to deduce the energy of stacking faults in wadsleyite. These calculated stacking-fault energies can then be compared with values inferred from transmission electron microscopy.

Table 6. Calculated interaction energy terms (in kJ mol<sup>-1</sup>)

|                  | P1a        | P4a      |
|------------------|------------|----------|
| J <sub>1</sub>   | -24.17     | -66.26   |
| J <sub>2</sub>   | -10.84     | -37.27   |
| J <sub>3</sub>   | 8.62       | 0.29     |
| J <sub>4</sub>   | 5.56       | -0.77    |
| E <sub>(∞)</sub> | -19 584.61 | -8621.11 |

The perfect wadsleyite structure has a stacking code

$$\dots \uparrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\downarrow \dots \quad (11)$$

The structure and hence the stacking code can be locally altered by the introduction of a stacking fault. Wadsleyite has been observed frequently to carry stacking faults of the type 1/2[101](010) (Price, 1983*b*; Madon & Poirier, 1983), which locally modify the structure so that its stacking code is described by

$$\dots \uparrow\uparrow\downarrow\downarrow\downarrow\uparrow\uparrow \dots \quad (12)$$

If (5) is valid, the energy of one such stacking fault can be calculated by determining the difference in the interaction energy that it introduces. For interactions up to and including the fourth neighbours, it follows from Table 5 that the ground-state energy per *N* spinelloid layers of the perfect wadsleyite structure is

$$E_{(2)} = 0.5NJ_1 + NJ_2 + 0.5NJ_3 + NE_{(\infty)}. \quad (13)$$

The development of a 1/2[101](010) stacking fault in wadsleyite changes this energy to

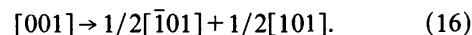
$$E_{(2)} = (0.5N + 1)J_1 + (N - 2)J_2 + (0.5N - 1)J_3 + 4J_4 + NE_{(\infty)}, \quad (14)$$

giving a zero-temperature stacking-fault energy of

$$E_{\text{FAULT}} = J_1 - 2J_2 - J_3 + 4J_4. \quad (15)$$

Using the values of J<sub>*i*</sub> from Table 6 to evaluate (15), the potentials P1a and P4a predict values for the 1/2[101](010) stacking-fault energy of 11.13 and 4.94 kJ mol<sup>-1</sup> respectively. Normally stacking-fault energies are expressed in terms of a surface energy, σ, with units of energy per area. The stacking fault considered lies on (010), which has a unit-cell cross-sectional area of 5.6 × 8.3 Å<sup>2</sup>. The calculated stacking-fault energies can consequently be re-expressed in appropriate units as 40 and 18 mJ m<sup>-2</sup> respectively.

In wadsleyite, stacking faults of the type 1/2[101](010) occur between the two partial dislocations that form when a [001](010) dislocation dissociates thus (Price, 1983*b*; Madon & Poirier, 1983):



An array of such dissociated dislocations, with leading and trailing partials linked by a length of 1/2[101](010) stacking fault, is shown in Fig. 2. The



equilibrium distance between the leading and trailing partial dislocation depends upon the surface energy,  $\sigma$ , of the stacking fault that links them, according to the well known relationship (e.g. Hull, 1968)

$$d = G\mathbf{b}_1 \cdot \mathbf{b}_2 / 2\pi\sigma, \quad (17)$$

where  $d$  is the distance between the trailing and leading partials,  $G$  is the shear modulus of the phase, and  $\mathbf{b}_1 \cdot \mathbf{b}_2$  is the dot product of the Burgers vectors of the two partial dislocations. From transmission electron microscopic observations such as the one shown in Fig. 2,  $d$  typically has a value of 1000 Å. For wadsleyite,  $G = 0.115$  TPa and  $\mathbf{b}_1 \cdot \mathbf{b}_2 = 9.2$  Å<sup>2</sup> for the two partial dislocations concerned. The resulting value for the energy of a  $1/2[101](010)$  stacking fault, inferred from transmission electron microscopy, is therefore  $17$  mJ m<sup>-2</sup>. The agreement between the stacking-fault energies inferred from lattice-simulation calculation and those deduced from electron microscopy is excellent, and strongly supports the view that the calculated values of the interaction energy between spinelloid units are meaningful and accurate.

### 5. Discussion

The calculations described above support the assumptions made by Price (1983a), Smith *et al.*

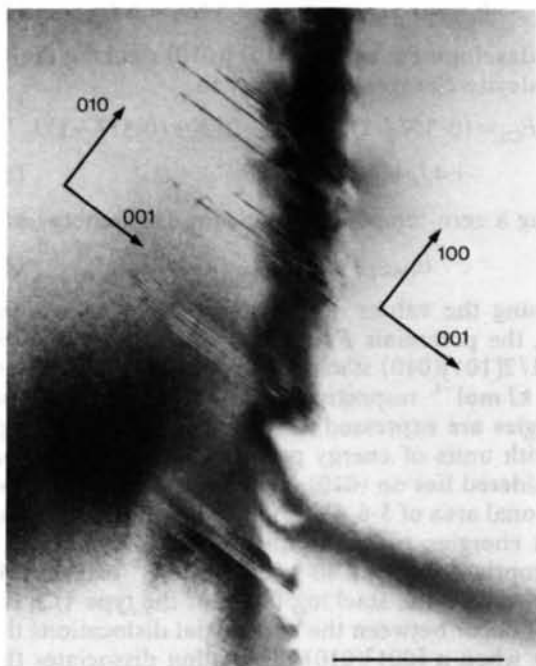


Fig. 2. Stacking faults of the type  $1/2[101](010)$  in wadsleyite formed by the dissociation of  $[001]$  dislocations into  $[\bar{1}01]$  and  $[101]$  partial dislocations. The dislocations occur on a subgrain boundary between two wadsleyite grains that are topotactically related. The wadsleyite microstructures are more fully described by Price (1983b).

(1984) and Price & Yeomans (1984) that the systematics of polytype energetics are described by (6). The approaches of these workers to the analysis of polytypism were similar yet distinct. They all analysed the energies of polytypic structures in terms of the interaction energies between component units, but chose to neglect different terms in their descriptions of the factors that determine which polytypic modifications are adopted. Price (1983a) chose not to consider explicitly the effect of temperature on the stability of polytypic phases, but explained the variety of observed polytypic modifications in terms of ground-state diagrams of a model with first-, second- and third-nearest-neighbour interactions. Smith *et al.* (1984) and Price & Yeomans (1984) chose to ignore the effect of interactions between third and further neighbours, but explicitly included entropic effects by considering non-zero temperatures. The results of the computer simulation described above suggest that a combination of the two approaches may best model polytypism in the magnesium silicate spinelloids.

In the ANNNI model, considered by Smith *et al.* (1984) and by Price & Yeomans (1984), the development of complex polytypic structures is predicted to occur only at elevated normalized temperatures. In this model, the normalized temperature ( $T_N$ ) can be defined in terms of the absolute temperature ( $T$ ) and  $J_0$ , the interaction energy between units within the polytypic layer, thus:

$$T_N = RT/J_0, \quad (18)$$

where  $R$  is the gas constant. If we assume that  $J_0 \approx J_1$ , then for the magnesium spinelloids considered above, physically reasonable temperatures (e.g.  $\sim 1000$  K) would correspond to normalized ANNNI model temperatures of between  $\sim 0.1$  and  $\sim 0.3$ . It therefore appears that the approximation made by Price (1983a) is not strictly valid, and that the role of temperature should not be ignored when considering the stability of spinelloid stacking sequences. This range of normalized temperature is within the range in which the low-temperature expansions used to determine the ANNNI phase diagrams are expected to be valid. In addition, analysis of the ANNNI model predicts that in this temperature range simple polytypic phases such as  $\langle 2 \rangle$ ,  $\langle 12 \rangle$  and  $\langle 1 \rangle$  should dominate over the more complex phases, in keeping with the structural simplicity of the observed magnesium silicate spinelloids. It should be pointed out, however, that the approximation made by Smith *et al.* (1984) and by Price & Yeomans (1984) is unlikely to be valid either. Although calculations based on potential  $P4a$  indicate that  $J_3$  and  $J_4$  are almost vanishingly small, potential  $P1a$  indicates that these terms may still be significant. Preliminary studies of an axial Ising model with interactions up to third neighbours (Baretto & Yeomans, private communication) show that very similar phase sequences occur for  $J_3 \neq 0$  as



for the ANNNI model.  $\langle 1 \rangle$ ,  $\langle 2 \rangle$  and  $\langle 3 \rangle$  are now ground-state phases (Price, 1983a), and  $\langle 12 \rangle$  together with a sequence of higher-order phases are stable at finite temperatures near the  $\langle 1 \rangle$ : $\langle 2 \rangle$  boundary. Indeed, for  $J_3 \neq 0$ , the phase  $\langle 12 \rangle$  occupies a more extended region of the phase diagram than for  $J_3 = 0$ . Therefore, the existence of higher-order interactions does not invalidate the picture presented by Smith *et al.* (1984) and Price & Yeomans (1984).

We may conclude that the results obtained from the computer simulations performed in this study have been successfully used to test the validity of the assumptions made in theoretical analyses of polytypism. Our calculations have revealed that the models discussed are essentially sound and that polytypism in spinelloids is probably best described by combining the two approaches to include the effect both of temperature and of further-neighbour interactions. It is hoped that in the future similar computer-based investigations will be used to test and refine theoretical solid-state physics and crystal chemical models that describe systems that are not amenable to direct experimental investigation.

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