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# Order-disorder in omphacitic pyroxenes: A model for coupled substitution in the point approximation—Reply

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## INTRODUCTION

Cohen's (1988) discussion covers three general topics, which we discuss in order: (1) appropriateness or ad hoc character of the generalized pair approximation (GPaA; Cohen, 1986) and generalized point approximation (GPA; Davidson and Burton, 1987)—ground-state analysis, symmetry constraints, and frustration; (2) the importance of short-range order, SRO; (3) additional contributions to the internal energy—long-range strain or electrostatic vs. short-range interactions. Although we discuss these areas separately, the same refutation applies to all three categories.

## GPaA vs. GPA

The GPaA expression for configurational entropy is inconsistent with the geometries of $C2/c$ and $P2/n$ omphacites and therefore yields incorrect results. Calculations based on the short-range-ordering energies of Cohen and Burnham (1985) and the GPaA predict geometrically impossible pair probabilities at 0 K and at experimentally and geologically relevant temperatures. The GPaA includes SRO, but only at the cost of making the statistical mechanics inconsistent with the geometry of the problem. We note that Cohen (1986; p. 183) wrongly asserts that "A *higher order* approximation, *different relative energies,* or quantitative consideration of strain contributions is *required* to account for the $C2/c$ to $P2/n$ transition in omphacites" (italics ours). Davidson and Burton (1987), however, proved that the *lower order* GPA is sufficient to account for this transition with the *same relative energies* and without consideration of strain contributions. Success of the GPA does not derive from imposing "ad hoc" constraints, ignoring SRO, or using an incomplete model for the internal energy; it is the natural consequence of including the geometry of the problem.

The cluster variation method (CVM) is a hierarchical prescription for counting the number of ways of configuring a system with a given energy, i.e., deriving an approximate expression for the configurational entropy. The hierarchy of CVM approximations proceeds from points (GPA = lowest-order) to pairs (GPaA) to triangles, and so on. The CVM entropy expression explicitly includes information about the symmetry, connectivity, and local geometry of the crystal structures involved. If the largest clusters that one chooses (points, pairs, . . .) exclude essential structural information such as frustration, then it is possible to obtain a counting that violates space-group symmetry and/or crystal-structure geometry (as occurs in the GPaA). This problem is well known in connection with CVM models of frustrated systems based on face-centered cubic (fcc) structures; e.g., Cu-Au, the fcc Ising ferromagnet, and fcc Ising antiferromagnet: (1) The point approximation for Cu-Au yields correct 0-K behavior, but incorrectly predicts second- rather than first-order transitions between the ordered and disordered phases (Kikuchi, 1977). (2) The pair approximation for Cu-Au and for the Ising antiferromagnet predicts that no ordered phase is stable (Kikuchi and Sato, 1974). (3) The triangle and octahedron approximations for the fcc Ising ferromagnet yield expressions for $T_c$ (critical temperature) that have no real roots, and for the Cu-Au system, no stable ordered phases are predicted (Aggarwal and Tanaka, 1977; Kikuchi, 1977). (4) The tetrahedron, tetrahedron + octahedron and double-tetrahedron + octahedron approximations, however, yield quite good results for the fcc Ising ferromagnet and Cu-Au systems (Aggarwal and Tanaka, 1977; Sanchez and deFontaine, 1978; Sanchez et al., 1982).

The results of CVM approximations for omphacite are similar to those for the fcc-based systems: (1) The GPA correctly predicts 0-K behavior and high-temperature phase relations but ignores SRO. (2) The GPaA fails for the same reasons that the pair approximation fails in the fcc case. (3) Higher-order approximations based on four-body (Burton, 1983) and eight-body clusters (2 × 8A; Burton, unpub. calculations) predict appropriate SRO, 0-K behavior, and phase diagrams.

**Summary.** Higher-order CVM approximations do not yield improved results if they are based on inappropriate clusters, and in the case of omphacite, pairs are clearly inappropriate. Higher-order approximations do yield improved results if, and only if, they are based on clusters that include essential structural information.

## GROUND-STATE ANALYSIS AND FRUSTRATION

A ground-state analysis based on the Cohen and Burnham (1985) SRO energies indicates that at 0-K, $P2/n$ omphacite is more stable than a mechanical mixture of diopside + jadeite by about −32 kJ/mol ($M1M2Si_2O_6$/mol), i.e.,

$$E_0 = E_{T=0,\mathrm{Omph}} = E_{\mathrm{Omph}} - (E_{\mathrm{Di}} + E_{\mathrm{Jd}})/2)$$
$$= -32 \text{ kJ/mol.}$$

The condition for 0-K stability of $P2/n$ omphacite in any model based on these parameters is

$$E_0 \leq 0,$$

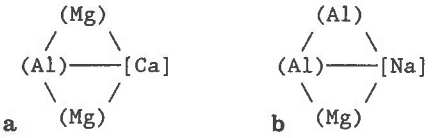
and this condition is *independent* of the statistical mechanics. If the GPaA were consistent with this energy model and the crystal structures, it would predict a $C2/c \rightarrow P2/n$ transition with $0 < T_c < \infty$. Failure of the GPaA to predict this transition, even though $E_0$ is less than 0, indicates that the GPaA is an inadequate approximation. It is not sufficient to find a set of parameters for which the GPaA predicts the transition, as Cohen (1986) suggests; this prediction must hold for any and every set that satisfies the condition $E_0 \leq 0$, or the theory is *internally inconsistent.* For any given parameterization of the internal energy, there is a correct model solution; i.e., a correct sequence of phase transitions and a correct phase diagram, regardless of their correspondence to a real system. The GPaA yields an incorrect solution for the parameterization based on SRO energies, and it will give an incorrect solution for any parameterization that involves frustration.

We agree with Cohen (1988, p. 910) that the GPaA fails because frustration is not included and that the result he describes as "complete short-range order and no long-range order" is "unphysical." We disagree, however, with his conclusion that the GPaA is nonetheless an adequate model for SRO in the $C2/c$ phase. The GPaA predicts geometrically forbidden values for the configurational internal energy ($\langle E \rangle < E_0$) that persist to about 1660 K and geometrically forbidden pair probabilities that persist from 0 K to about 2025 K, which is above the 40-kbar solidus [Bell and Davis, 1969; for parameters that are scaled by a factor of 3.4 to give $T_c = T_c\ (2 \times 8\text{A}) = T_c$ (Cohen's Monte Carlo result) = 1123 K, the value estimated by Carpenter, 1981].

We thank Cohen for clarifying the definitions of the SRO energies presented in Cohen and Burnham (1985); previously, we had underestimated their magnitudes by a factor of four. We emphasize, however, that this correction does not affect our comparison of observations to calculated phase-diagram topologies, which depend only on the relative values of these parameters. Nor does it affect our optimization of energy parameters, for which we used Cohen and Burnham's parameters divided by four as starting values. Finally, as discussed above, this correction is insufficient to rehabilitate the GPaA.

## SHORT-RANGE ORDER

The GPaA predicts simultaneous concentrations of Mg-Al, Mg-Na, and Al-Ca pairs that are mutually inconsistent. The formation of an energetically favorable Mg-Al pair in the system implies the formation of *at least as many*[1] unfavorable Mg-Na or Al-Ca pairs (Fig. 1), which leads to the constraint



Figs. 1a and 1b. Clusters of nearest-neighbor (nn) M sites in the $C2/c$ and $P2/n$ omphacite structures, (Mg) = Mg on M1, [Ca] = Ca on M2, etc. Ordering of Mg and Al on M1 requires the formation of unfavorable (Al)–[Ca] and (Mg)–[Na] nn pairs.

$$N_u \equiv N_{\text{Mg-Na}} + N_{\text{Al-Ca}} \geq N_{\text{Mg-Al}}, \qquad (1)$$

where $N_u$ is the number of unfavorable M1-M2 pairs, $N_{\text{Mg-Al}}$ is the number of favorable Mg-Al pairs and so on. Using Cohen's notation for SRO parameters,

$$N_u = 3N_0[P_{\text{Mg-Na}} + P_{\text{Al-Ca}}] = 3N_0(1 - \sigma_3) \qquad (2)$$

and

$$N_{\text{Mg-Al}} = N_0(P_{\text{Mg-Al}} + P_{\text{Al-Mg}}) = N_0(1 + \sigma_1), \qquad (3)$$

where $N_0$ is Avogadro's number, and the factor of three is present in Equation 2 because there are three times as many M1-M2 pairs as M1-M1 pairs in the system. Substituting Equations 2 and 3 into 1, we see that $\sigma_1$ and $\sigma_3$ are constrained by the inequality

$$2 - 3\sigma_3 \geq \sigma_1. \qquad (4)$$

Note that Cohen's GPaA yields $\sigma_1 = 0.77$ and $\sigma_3 = 0.7$ at 1010 K in clear violation of Inequality 4.

We agree that SRO is important in this system, but it is not essential for the enumeration of possible phase-diagram topologies, and this was the purpose of Davidson and Burton (1987). We presented the simplest formulation that allows such an enumeration (the GPA). Consistency of the configurational entropy expression with the $C2/c$ and $P2/n$ pyroxene structures is a first-order qualitative requirement for any reasonable model. Including SRO yields a second-order quantitative improvement, but only if the SRO conforms to the geometry of the problem.

**Summary.** (1) The GPA is the simplest *adequate* model for order-disorder in omphacite or for phase relations of the jadeite-diopside join, but it ignores SRO. (2) The GPaA is the simplest model that includes SRO, but the predicted SRO is geometrically impossible. The GPaA also fails to predict an ordered phase, so it is *inadequate* for phase-diagram or phase-transition calculations. (3) A correct treatment of SRO in omphacite requires an approximation that is based on clusters larger than pairs; e.g., the 2 × 8A predicts SRO that is consistent with omphacite geometry, and $T_c\ (2 \times 8\text{A})$ is within the uncertainty of Cohen's Monte Carlo value.

## ADDITIONAL CONTRIBUTIONS TO INTERNAL ENERGY

Cohen's discussion of strain, electrostatic, and other long-range contributions to the internal energy is irrelevant to a comparison of the GPA and GPaA. The differ-

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[1] If it were possible to make configurations in which the number of Mg-Al pairs exceeded the number of unfavorable Mg-Ca and Al-Na pairs, then the system would have a different groundstate.

ence between these approximations is in their expressions for the configurational entropy (how the number of ways of configuring the system is counted), not in their models for internal energy. Long-range energy terms can (and perhaps should) be added to both models, but these terms cannot correct the erroneous GPaA expression for the configurational entropy. The accuracy or completeness of a given set of energy parameters is not the issue. The issue is: given a particular set, does the approximation yield a correct (geometrically allowed) solution?

We note that Cohen's example for the importance of strain energy is one in which the strain-free $\epsilon$ diagram yields much better agreement with experiment than the $\epsilon$-$G$ diagram (cf. Cohen's Fig. 1 with Figs. 8 and 9 in Kikuchi, 1977). Also, the $\epsilon$ and $\epsilon$-$G$ diagrams he shows are *topologically equivalent*: they both have the same stability fields; only the relative areas of the fields are different.

## CONCLUSIONS

The GPaA (Cohen, 1986) fails because its configurational entropy expression is inconsistent with the $C2/c$ and $P2/n$ pyroxene structures, not because additional contributions to the internal energy are required. The point approximation succeeds because its configurational entropy expression is consistent with $C2/c$ and $P2/n$ pyroxene structures, not because it ignores SRO, or additional energy terms. There is nothing "ad hoc" about making the statistical mechanics conform to the geometry of the system. The GPaA predicts geometrically impossible values for $\langle E \rangle$ and SRO at 0 K and at temperatures of experimental or geologic interest. Additional terms in the internal-energy expression cannot correct the erroneous GPaA expression for configurational entropy, nor do they provide a basis for comparing the GPaA and GPA. An adequate treatment of SRO in omphacitic pyroxenes requires an approximation that is based on clusters larger than pairs.

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