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

RONALD E. COHEN

Naval Research Laboratory, Code 4684, Washington, D.C. 20375-5000, U.S.A.

ABSTRACT

The differences between the generalized pair approximation and the Bragg-Williams approximation are discussed for omphacitic pyroxenes [$CaMgSi_2O_6$ (diopside)–$NaAlSi_2O_6$ (jadeite)]. At low temperatures, the pair approximation predicts an unrealistic state with complete short-range order and no long-range order for omphacite. The Bragg-Williams approximation does not give this result because it includes no short-range order and thus is constrained to give an ordered ground state. For any finite cluster size, the cluster variation method (CVM) gives unphysical low-temperature properties for systems without long-range order; in other words it is not a good approximation for spin-glass type systems.

Recent CVM calculations for ionic-covalent carbonates, oxides, and silicates use incomplete expressions for the total energy, since they ignore long-range interactions. The energy should contain long-range elastic and electrostatic contributions that are dependent on the state of long-range order and composition as well as the short-range order contributions. These interactions are expected to be particularly important in coupled solid solutions, such as omphacitic pyroxenes. Neglect of these long-range contributions in general leads to energy parameters that have no physical meaning.

INTRODUCTION

The purpose of statistical mechanical modeling of solid solutions is to understand better and predict thermodynamic solution properties. Statistical mechanical modeling also gives guidance for the formulation of empirical models; a functional form that is based on physics should behave better than *ad hoc* models for interpolation and extrapolation. Phase equilibria can then be calculated from the thermodynamic formulations. Cohen (1986a, 1986b, 1986c) and Cohen and Burnham (1985) addressed the problem of short-range ordering in aluminous pyroxenes and the effects of short-range ordering on the thermodynamic properties. A large degree of short-range order is expected in coupled solid solutions such as aluminous pyroxenes since ions of different valence mix in these crystals. An understanding of coupled solid solutions is particularly important because pyroxenes and feldspars, the most abundant minerals in the Earth's crust, are coupled solid solutions.

Davidson and Burton (1987) have suggested that the Bragg-Williams (BW) (1935a, 1935b) approximation is superior to the generalized pair approximation presented in Cohen (1986b). Their criticism of the pair approximation is its behavior at low temperatures (0 K). In fact, the pair approximation does not predict reasonable probabilities for the M1-M2 pairs even at moderate temperatures. The pair approximation is not sensitive to structural details larger than the pair, and this fact leads to greater ordering between M1 and M2 than is consistent with the pyroxene structure. It will be shown that only

the crudeness of the BW approximation saves it from similar behavior. The utility of the BW approximation relative to the pair approximation depends on the problem addressed. The pair approximation is not appropriate to study the long-range ordering transition in omphacite, since no transition is found. On the other hand, the BW approximation is not appropriate to study short-range order, since it is assumed that no short-range order is present. Cohen (1986a, 1986b, 1986c) concluded that the random model for the entropy, that is, the entropy formulation of the BW model, is generally sufficient as a first approximation in describing the thermodynamic properties of coupled solid solutions.

Regardless of what approximation method is used for the entropy, the expression for the energy is critical if one wants to obtain physically meaningful results. Davidson and Burton have neglected the probable importance of long-range interactions. Such interactions would change the possible phase-diagram configurations, as well as the configurational thermodynamic properties.

COMPARISON OF THE BRAGG-WILLIAMS MODEL AND THE PAIR APPROXIMATION FOR OMPHACITES

In the BW approximation, there is no short-range order. The probability of simultaneously finding an A atom on one site and a B atom on another site is simply the product of the individual site-occupancy probabilities. For example, if the site-occupancy fraction of atom type A on site 1 is 0.5 (i.e. $N_A^1 = 0.5$), and similarly for atom type B on site 2, then the probability of finding an AB

pair on sites 1 and 2 is simply 0.25 (or $P_{AB}^{12} = 0.25$). In other words, in the BW approximation, there is no short-range order other than that dictated completely by the long-range order. If the crystal is long-range ordered so that $N_A^1 = 0.25$ and $N_A^2 = 0.75$, then $P_{AB}^{12} = 0.1875$. Clearly the BW approximation is not a very good approximation if the goal is to study the effects of short-range order, since short-range order is not independently variable. In $C2/c$ pyroxenes, for example, the BW approximation assumes that the arrangement of atoms on each site is completely random. Almost all thermodynamic solution models for pyroxenes prior to Cohen (1986a, 1986b, 1986c) assumed a large degree of short-range order in omphacites. This assumption could not be tested within the BW approximation. The pair approximation is the simplest model that includes short-range order.

All analytic techniques for calculating phase diagrams and configurational thermodynamic properties from a microscopic viewpoint involve approximations. The utility of a particular method depends on the problem being addressed. There are only two essential differences between the pair approximation and the BW model. First, the pair approximation allows for short-range order, which is described by a set of short-range order parameters. Second, the expression for the entropy in the pair approximation contains information on the crystal structure for both pairs and crystallographic sites, whereas the BW approximation contains information only on the relative numbers of crystallographic sites. Both the pair approximation and the BW model give incorrect or unphysical results for particular properties.

The pair approximation gives configurations for the M1-M2 pairs in omphacite that are too ordered to be consistent with the pyroxene structure in the disordered $C2/c$ structure. At 0 K, the pair approximation gives a state with complete order of Al and Mg on M1 and complete order of NaAl and CaMg on M1 and M2. The ground state has a short-range order parameter, $\sigma_3 = P(\text{CaMg}) + P(\text{NaAl}) - P(\text{CaAl}) - P(\text{NaMg})$ of 1, whereas the maximum should be ⅓. [The two types of M1-M2 pairs are not distinguished here since the associated ordering energies were found to be equivalent in Cohen and Burnham (1985).] This result occurs because the interactions between M1 and M2 are *frustrated* (Toulouse, 1977); that is, there is no way to order favorably all of the M1-M2 pairs because each M1 has three M2 next-nearest neighbors and vice versa. The short-range order parameter should only reach ⅓ owing to the formation of unfavorable Ca-Al and Na-Mg pairs. The pair approximation, however, does not include this information and therefore does not include frustration. The result can be demonstrated easily for $\text{Di}_{50}\text{Jd}_{50}$. Using the ordering energies calculated in Cohen and Burnham (1985, Table 3), an unphysical state of complete short-range order of Na-Al, Ca-Mg, Ca-Na, and Mg-Al gives an ordering energy of −136 kJ/mol. However, for the $P2/n$ ordered omphacite, the short-range order parameter for the reaction between Ca and Na on M2, with Mg and Al on M1, reaches a

maximum of ⅓ at the low-temperated limit owing to the imposed long-range order. This gives an ordering energy of −76 kJ/mol. The $C2/c$ state is energetically favored. [The scaling factor (Cohen and Burnham, 1985; Cohen, 1986b) is neglected here; it would reduce the difference in energies by a factor of about 5.5.] It is only the impossibility of achieving short-range order in the BW approximation that makes it appear sensitive to the frustration.

At higher temperatures, the ordering between M1 and M2 can be higher than $\sigma_3 = ⅓$ because of the disorder in the M1 and M2 chains. To examine the physical limits, simulated annealing calculations (Press et al., 1986) were performed. For $X_{Jd} = 0.5$, the pair approximation gives $\sigma_1(\text{M1M1}) = 0.77$, $\sigma_2(\text{M2M2}) = 0.28$, and $\sigma_3(\text{M1M2}) = 0.70$ at a reduced temperature of 1 (approximately 1000 K). The closest configuration to the calculated short-range order parameters of the pair approximation was found to be $\sigma_1 = 0.66$, $\sigma_2 = 0.28$, and $\sigma_3 = 0.44$. For compositions displaced from the center of the join, the physical bounds are higher for σ_3. For $X_{Jd} = 0.25$, the pair approximation gives $\sigma_1 = -0.02$, $\sigma_2 = -0.11$, and $\sigma_3 = 0.75$, whereas the closest configuration found gives $\sigma_1 = -0.06$, $\sigma_2 = -0.12$, and $\sigma_3 = 0.68$. Finally, in the dilute limit, agreement is found between the pair approximation and an exact solution (Cohen, 1986b).

These results are not surprising since the pair approximation contains information only about the numbers of pairs, not the detailed way that the pairs are connected. Since the M1-M2 pairs are too ordered, the free energy of the disordered $C2/c$ phase is too low and is always lower than the free energy of the ordered $P2/n$ phase, using the ordering energies from Cohen and Burnham (1985). By varying the energies as described in Cohen (1986b, Fig. 15), the experimentally observed $P2/n$ field can be made to appear, but it becomes unstable with respect to $C2/c$ at still lower temperatures. This low-temperature $C2/c$ phase is unphysical, however; the pair approximation gives negative configurational entropy for the $C2/c$ phase at low temperatures.

The cluster variation method (CVM) contains contributions to the entropy of both positive and negative sign. At infinite temperature, the configurational entropy of the CVM is equal to that of a random distribution of atoms on each site. At 0 K, however, the calculated entropy is in general negative unless all of the cluster probabilities are either zero or one. This is true for any finite cluster size except the point, which is only a member of the CVM hierarchy as a limiting case since it does not contain positive and negative contributions to the entropy. Thus the CVM cannot in general be expected to give realistic ground-state properties for frustrated systems, except in the case of phase separation.

As discussed in the reply by Burton and Davidson (1988), similar behavior of the pair approximation is found in other systems. In the CuAu system, for example, the pair approximation does not predict a phase transition to an ordered superlattice because the pair approxi-

mation underestimates the free energy of the disordered phase (Kikuchi and Sato, 1974). At the CuAu composition, the pair approximation gives a ground state in which every Cu is surrounded by twelve Au atoms and vice versa, which is not geometrically possible on the FCC lattice. Though the BW approximation does give phase transitions in the CuAu system, it gives a qualitatively incorrect phase diagram (de Fontaine and Kikuchi, 1978).

The BW approximation cannot give pair probabilities inconsistent with the pyroxene structure, because in the BW approximation there is *no* short-range order if there is no long-range order. This is an advantage of the BW approximation, particularly if one is interested in the long-range-ordered phase. However, if one is interested in the $C2/c$ phase, the BW approximation is of very little use in estimating pair probabilities unless one has some reason to expect very little short-range order. The BW model gives short-range order parameters of zero for $X_{Jd} = 0.5$ and zero configurational heat capacity. The BW model overestimates the free energy of a disordered phase, whereas it describes a long-range-ordered phase rather well. Thus it overestimates the temperature for an order-disorder phase transition by up to a factor of two (de Fontaine, 1979). It is not surprising, therefore, that the long-range ordering in omphacite is found using the BW approximation.

The entropies, enthalpies, and free energies of the $C2/c$ phase calculated in the pair approximation are probably considerably closer to the exact solution than the BW values at moderate temperatures. The short-range order parameters σ_1 and σ_2 are probably quite accurate in the pair approximation, as well, since they refer to one-dimensional chains and the pair approximation is exact for one-dimensional chains.

One could conceivably formulate a form of pair approximation that had the frustration effect built in and that would give a reasonable result for the 0-K ordered state. However, such a model would be *ad hoc* and would not flow naturally from the pair approximation. The formulation of the entropy in the pair approximation is unique, so that only a constraint on the pair probabilities could be considered. One way to fix the low-temperature behavior would be to constrain the short-range order parameter for the ordering between M1 and M2, so that for $Di_{50}Jd_{50}$ it could reach a maximum of $1/3$ for the disordered $C2/c$ phase as well as the ordered $P2/n$ phase. This seems reasonable, but it would lead to discontinuities in the heat capacity at the temperature at which the boundary is reached. Such a model would give identical properties as calculated with the unconstrained generalized pair approximation for temperatures above this temperature.

Note that frustration is not a factor in the fassaitic pyroxenes, so the pair approximations for fassaites and CaTs (Cohen, 1986b) are probably considerably more reliable than those for omphacites.

Problems with the formulation of the energy are more serious than those associated only with the low-temper-ature behavior. They affect all of the CVM calculations that have been presented in the past for ionic-covalent crystals such as carbonates (Burton and Kikuchi, 1984; Burton, 1987) and ilmenites (Burton, 1985), as well as pyroxenes (Davidson and Burton, 1987).

FORMULATION OF THE ENERGY

In simple substitutional alloys, with little "lattice mismatch" and only small charge transfer, the energy as a function of composition and state of order can be represented quite well by a sum of short-range interaction energies. These interaction energies may be simple pairwise interactions, or they may be cluster interactions for larger clusters of atoms (de Fontaine, 1979).

If, however, there is a significant difference in the effective sizes of the atoms substituting for each other, there is a contribution to the energy that cannot be written in this form no matter how many parameters are included and no matter how large the cluster. This contribution arises because the mismatch leads to elastic contributions to the energy that are long-range in nature and cannot be approximated as short-range sums. Kubo (1985) discussed this effect for Cu-Zn (brass) and showed that a reciprocal-space formulation leads to a correct description of the effects of elastic strains produced by lattice mismatch. It may be possible to find a set of short-range energy parameters by fitting the experimentally determined phase diagram. Such energy parameters, however, do not represent any real physics since the formulation itself is faulty.

Mbaye et al. (1987) and Ferreira et al. (1987) have considered this effect and have found not only that the elastic contributions can be quite large, but that the form of the phase diagram can be drastically modified when elastic interactions are included. In Figure 1, their results are reproduced for the Cu-Au system (Ferreira et al., 1987). The difference between Figures 1a and 1b is entirely due to the inclusion of long-range elastic interactions in 1a. Similar results were found for the (In,Ga)P system (Mbaye et al., 1987); therefore, the elastic interactions are important regardless of the type of bonding.

They also found the general result that elastic strain leads to stabilization of ordered phases and to destabilization of the disordered phase. The elastic energy, which was not calculated in Cohen and Burnham (1985) because of the lack of a sufficiently accurate model, would destabilize the $C2/c$ disordered phase and stabilize the ordered $P2/n$ phase.

In complex crystal structures, inhomogeneous deformations also contribute to the energy as functions of order and composition and are included here as part of the strain energy. Even if the lattice parameters vary little with state-of-order, the inhomogeneous contributions can be significant and have a complicated form.

Ionic-covalent crystals also contain large long-range electrostatic forces. In coupled solid solutions where ions of different valence mix, long-range contributions to the energy as functions of composition and state-of-order are
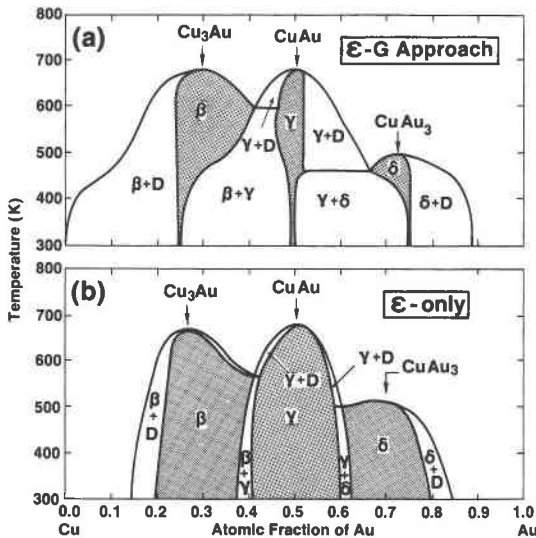
Fig. 1. Phase diagrams for the Cu-Au system. (a) Both configurational and long-range elastic interactions are included. (b) Only the configurational interaction is included. Clearly the long-range elastic interactions are important. From Ferreira et al. (1987).

Fig. 2. Excess configurational enthalpy as a function of composition and reduced temperature ($-RT/W_{M1-M1}$) calculated from the generalized pair approximation. A reduced temperature of 1 corresponds to 1010 ± 240 K. The difference between the experimental excess enthalpies and the calculated configurational enthalpy is an estimate of the long-range contributions to the total enthalpy. From Cohen (1986b).

expected to be particularly acute. Cohen and Burnham (1985) found, surprisingly, that in spite of the long-range nature of the forces, the ordering energy at fixed composition and fixed strain could be approximated very well by a simple short-range pair formulation. However, this was not true for the energies as a function of composition. Cohen (1986b) did not calculate phase diagrams since the energy as a function of composition must be accurate in order to calculate the coexistence of phases of different compositions. Cohen discussed the expression for the energy (Cohen, 1986b, Eq. 11) and suggested that the energy can be broken up into a part that depends explicitly only on the short-range order parameters, H^c, a part that depends only on the composition, H^x, a part that explicitly depends only on the long-range order parameters, H^L, and a temperature dependent part not included in the other terms, H^v. Ferreira et al. (1987) have shown that the first two of these contributions can indeed be rigorously separated. (They use ϵ for contribution H^c and G for contribution H^x.) There is a part dependent on the state of long-range order as well since long-range ordering leads to long-range elastic strains, and the temperature-dependent term comes in through the changes in vibrational state with order and composition. Cohen and Burnham (1985) only calculated the term H^c; therefore, a phase diagram could not be calculated. H^c and H^x are expected to be the dominant terms, and H^v is expected to be the smallest term. H^x was called the nonconfigurational contribution to the energy in Cohen (1986b) since it is not an explicit function of the order parameters.

Further evidence that the long-range contributions are significant is given in Figure 2, reproduced from Cohen (1986b). Figure 2 shows the calculated excess configura-
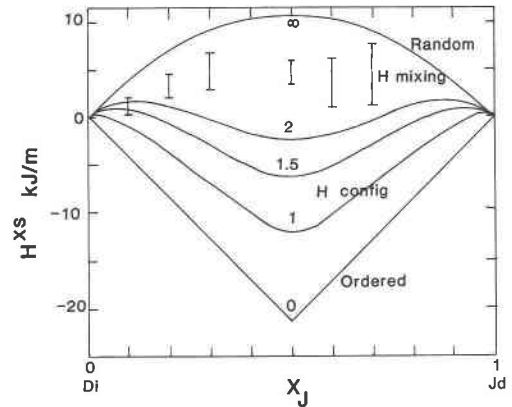
tional enthalpy, H^c, as a function of reduced temperature and composition. A reduced temperature of 1 corresponds to 1010 ± 240 K. Also shown are the experimental excess enthalpies from data of Wood et al. (1980) as reduced by Cohen (1986c). The term H^x (or G) can be estimated as the difference in the measured mixing enthalpies and the curve marked with a reduced temperature of 1. The long-range contributions are positive and are larger in magnitude than the short-range-ordering contributions. Some of the discrepancy, however, may be due to nonequilibrium disordered states in the synthesized pyroxenes, so that the long-range contributions to the energy are probably somewhat smaller than suggested in Figure 2.

Finally, Davidson and Burton (1987) use the short-range-ordering energies in Cohen and Burnham (1985) incorrectly. They identify W_1 and W_2 in Cohen and Burnham (1985) with their W^{M1} and W^{M2}, and $\frac{2}{3}W_3$ with ΔG^0_3 (Davidson, pers. comm.). In the completely disordered state with no short- or long-range order, the short-range order parameters defined in Cohen and Burnham are given by $-4x^2 + 4x - 1$. Comparison with Davidson and Burton's equation for H^{sol} with s_1 and s_2 equal to zero shows that W^{M1} is analogous to $4W_1$, and similarly for W_2 and W_3. For example, for completely disordered omphacite, the contribution from the M1-M1 pairs varies as $4x(1 - x)W_1$ in Cohen and Burnham's formulation, and as $x(1 - x)W^{M1}$ in Davidson and Burton's formulation. [This comparison is for formula units of the same size; note that they used a 12-oxygen formula unit rather than the 6-oxygen formula unit used in Cohen and Burnham.] This incorrect use of the energy parameters is the reason that Davidson and Burton obtain reasonable ordering temperatures without use of the effective dielectric constant used in Cohen (1986b). On the other hand, the ra-

tios $n = -\Delta G_0^{\circ}/(W^{M1} + W^{M2})$ and $r = W^{M2}/W^{M1}$ are not affected by their error of a factor of four. Nevertheless, even the relative ordering energies are not sufficient to calculate phase diagrams. The ordering energies calculated in Cohen and Burnham do not allow comparison of the energies of two different compositions. This is the reason Cohen (1986b) did not calculate phase diagrams.

RECENT PROGRESS

In order to examine the validity of the ordering energies calculated in Cohen and Burnham (1985) and to study the order-disorder phase transition in omphacite, Monte Carlo calculations (Binder, 1987) have been performed for omphacite. Unlike CVM calculations, Monte Carlo is exact for a given system size if sufficient configurations are included. Using the relative ordering energies in Cohen and Burnham (1985), a phase transition is found at a reduced temperature $-RT/W_1 = 0.85$, which corresponds to 850 ± 250 K. This temperature is a little lower than an experimental estimate of T_c of 1123 K (Carpenter, 1981), but certainly reasonable considering the simple model used to calculate the ordering energies. The pair approximation for CaTs was used to estimate the scaling of the energies (Cohen, 1986b), and the same scale factor gives a reasonable result for omphacite. Of course, there is no a priori reason to suspect that the same scaling factor would be applicable to minerals of different composition such as CaTs and omphacite. The consistency of the results, however, strongly suggests that the short-range order parameters and entropy of CaTs derived using the pair approximation do not contain the problems that the pair approximation encounters in frustrated systems. Thus it appears that the pair approximation is a good first approximation for short-range order in nonfrustrated systems.

CONCLUSIONS

The pair approximation gives an unrealistic ground state for omphacite because it does not include frustration. On the other hand, the BW approximation gives a reasonable result at low temperatures, but only because it is constrained to do so. The BW approximation also contains no information on short-range order, so it cannot be used to consider the effects of short-range order, which was the purpose of Cohen (1986a, 1986b, 1986c) and Cohen and Burnham (1985).

The energy formulation used in recent CVM calculations for ionic-covalent oxides and silicates is incomplete, because such solutions contain long-range elastic and electrostatic forces that cannot be realistically represented by a short-range formulation. Cohen and Burnham (1985), however, found that the ordering energies can be represented as short-range interactions written as stoichiometric chemical reactions between pairs. The fact that neglect of these contributions of the energy leads to reasonable phase diagrams within the BW approximation is proba-

bly fortuitous and is due to canceling errors in the energy formulation and the BW approximation.

In summary, it is not meaningful to state that either the pair approximation or the BW approximation is superior. It depends on the properties of the system in which one is most interested. Of the two approximations, the BW approximation is necessary for studying the long-range-ordering transition in omphacites, and the pair approximation is essential for investigating short-range order. Higher-order approximations are requisite for accuracy in phase diagrams and configurational properties. Regardless of the entropy formulation used, an inaccurate or incomplete formulation of the energy will lead to less useful results. This is particularly true when energy parameters are fit to give agreement with experiment.

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