CLUSTER EXPANSION OF fcc Pd-V INTERMETALLICS

D. de FONTAINE\textsuperscript{1,2}, C. WOLVERTON\textsuperscript{1,3}, G. CEDER\textsuperscript{1,2*} and H. DREYSSE\textsuperscript{4}

\textsuperscript{1}Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA
\textsuperscript{2}Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720, USA
\textsuperscript{3}Department of Physics, University of California, Berkeley, CA 94720, USA
\textsuperscript{4}Laboratoire de Physique du Solide, Université de Nancy, Vandœuvre-les-Nancy, France

ABSTRACT. A cluster expansion is used to compute fcc ground states from first principles for the Pd-V system. Intermetallic structures are not assumed but derived rigorously by minimizing the configurational energy subject to linear constraints. A large number of concentration-independent interactions are calculated by the method of direct configurational averaging. Agreement with the fcc-based portion of the experimentally-determined Pd-V phase diagram is quite satisfactory.

1. Introduction

In recent years, first-principles total electronic energy calculations have been remarkably successful in predicting heats of formation, lattice parameters, and elastic moduli of simple intermetallic compounds at their stoichiometric compositions and at zero Kelvin. Performing similar calculations for off-stoichiometric compositions, in disordered or partially ordered states, has obviously not progressed as rapidly, as it is required to solve combined quantum and statistical problems at a high level of accuracy.

One aim of such calculations is to derive, virtually from first principles, reasonable temperature-composition phase diagrams for binary metallic systems, say. Thermodynamic quantities, such as free energies, entropies, enthalpies, states of order may then be deduced as by-products of the calculations.

Over the last ten years or so, it has become apparent that the preferred way of investigating alloys computationally (ordered or disordered) is through the medium of expansions in cluster functions. The theoretical framework is rigorous, flexible and completely general, and is essential for formulating both the energy (E) and the configurational entropy (S), hence the free energy (F = E − TS).

The cluster expansion method can also be used to tackle the difficult problem of ground state determination. Predicting, without guesswork, which superstructures of a given lattice have minimum energy, is essential and is a topic which has perhaps not received as much attention lately as it deserves. In this article, we shall address precisely this problem, and, after having outlined the basic theory, we shall apply the cluster methods to the ground state determination of fcc superstructures in the Pd-V system.

*Present address: Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.
It was back in 1951 that Kikuchi [1] introduced the idea of clusters in the statistical thermodynamics of the Ising model as a way of improving systematically on the currently known approximations of the configurational entropy. Since the free energy was obtained, in Kikuchi's method, by minimizing a functional with respect to cluster variables, he called his hierarchy of approximations the cluster variation method (CVM). Its application to the calculation of phase diagrams was suggested by Van Baal [2] in 1973, and the use of the method has expanded considerably ever since.

The cluster method is now viewed as far more general than the early practitioners of the CVM probably envisaged. Today, clusters (on a lattice) are considered as the essential building blocks for any description of alloy properties which depend on configuration. This approach was first described in 1982, in a remarkable paper by Sanchez, Ducastelle and Gratias [3]. Although these authors treated the general multicomponent case, we shall here summarize results for binary systems only. An alternative and very elegant method of treating multicomponent systems was suggested by Finel [4] and was very recently described in a very clear and comprehensive review article by Inden and Pitsch [5].

In a binary alloy (AB) let the pseudo-spin variable \( \sigma_p = +1 \) (\(-1\)) stand for an A (B) atom at lattice site p. Consider now a set of lattice points \( \{p, p', p'', \ldots \} \) which we shall denote as "the cluster \( \alpha \)." It was shown [6,7] that cluster functions \( \varphi_\alpha(\sigma) \) can be constructed so as to form an orthonormal set in the space of \( 2^N \) configurations, \( N \) being the total number of lattice points. A convenient choice [3] is the direct product of \( \sigma \) variables on the cluster points:

\[
\varphi_\alpha(\sigma) = \sigma_{p_1} \sigma_{p_2} \sigma_{p_n} \ldots
\]

(1)

The set \( \{ \varphi_\alpha \} \) is orthonormal in the sense that the scalar product \( <\varphi_\alpha(\sigma), \varphi_\beta(\sigma)> \), defined as the normalized sum of the product \( \varphi_\alpha \varphi_\beta \) over all configurations, is unity if the two clusters \( \alpha \) and \( \beta \) coincide, zero otherwise. It follows that any function of configuration, \( f(\sigma) \), say, can be expanded in the set of cluster functions

\[
f(\sigma) = \sum_\alpha f_\alpha \varphi_\alpha(\sigma)
\]

(2)

with generalized Fourier coefficients given by

\[
f_\alpha = <\varphi_\alpha(\sigma), f(\sigma)>
\]

(3)

Of particular interest is the expectation value of the function \( f(\sigma) \), obtained by taking an ensemble average of Eq. (2) at given \( T \) and chemical field \( \mu \) (difference of chemical potentials \( \mu_B - \mu_A \)):

\[
< f > = \sum_\alpha f_\alpha \xi_\alpha
\]

(4)

where the \( \xi_\alpha \), denoted multisite correlation functions, are ensemble averages of the corresponding cluster functions. Eq. (4) is important in that, in principle, it shows how to express any