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The Role of the Cluster Variation Method in the First Principles Calculation of Phase Diagrams

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The Cluster Variation Method (CVM) proposed by Professor Kikuchi to study cooperative phenomena in solids has played a major role in the development of phenomenological and first principles theories of phase equilibrium. The CVM provides an accurate and rigorous framework for the study of the configurational thermodynamics of alloys. As such, the method has been a powerful tool in the quest for insight into the main contributions to alloy phase stability and in the interpretation of complex and extensive experimental data. The early successes of the CVM have also been instrumental in the development of ab-initio methods for the reliable description of phase equilibrium and, in particular, of phase diagrams. These new developments have relied heavily on the CVM and on the theoretical ideas put forth over 40 years ago by Professor Kikuchi. Here, we review the use of the CVM in the first-principles computation of phase diagrams, and present results for the Zr-Nb system. The theory that emerges is one that incorporates the calculation of total energies in the local density approximation, configurational entropies using the CVM, and vibrational modes in the Debye-Grüneisen approximation.

§ 1. Introduction

A strictly computational approach to alloy phase diagrams determination has recently emerged as a potentially valuable tool in the design and development of new materials. This relatively new thrust in computational materials science evolved from numerous early studies of simple phenomenological models. These models, based essentially on generalizations of the Ising Hamiltonian, reproduce quite well the most important features of alloy phase diagrams. The Cluster Variation Method (CVM) of Statistical Mechanics[1] played a key role in these studies since it provided an efficient and computationally economical way of describing the configurational thermodynamic of alloys.[2)~6)]

The early success of the CVM revived the old dream of computing alloy phase diagrams from first principles; i.e., from the knowledge of the alloy's electronic structure. Indeed, one of the most significant recent developments in alloy theory, density functional theory and its computational version, the local-density approximation (LDA),[7] was fully developed and ready to be applied together with the statistical models to tackle the delicate problem of alloy stability at finite temperatures.

The implementation of the local-density approximation, together with the development of efficient linear methods to study the electronic structure of solids, led to fully ab-initio calculations of the total energy at zero temperature of pure meals,8)~10) relatively simple compounds11),12) and disordered alloys.13)~15) These quantum mechanical total energy calculations reproduced a wide range of physical properties within a few percent of the experimental values, and provided conclusive evidence in favor of the local-density approximation.

The missing link between phase stability at finite temperatures and electronic structure was established by developments in the description of the configurational thermodynamics of alloys. These developments are closely related to the CVM. In the language of the CVM, the statistical thermodynamics of the alloy is described in terms of atomic configurations of clusters of lattice sites. This localized description of the state of partial order can be conveniently accomplished using multisite correlation functions.1),16) Specifically, it has been shown by Sanchez et al.16) that any function of configuration, of which the energy is only a particular case, can be expanded in terms of multisite characteristic functions, the expectation values of which are the correlation functions. Furthermore, the characteristic functions form an orthonormal basis in configuration space. Although the cluster expansion can be applied quite generally to any function that depends upon the configuration of the system, its usefulness rests heavily on the rate of convergence in terms of the size and complexity of the clusters.

The cluster expansion applied to the configurational energy results in the well known Ising-like bi-linear expression in terms of effective multisite interactions and correlation functions.16) Studies of binary and multicomponent alloys, whereby the multisite interactions were determined using ground state analysis and available thermochemical data, such as energies of formation, clearly established the usefulness of Ising-like models in the description of states of partial order. However, it should be emphasized that the rigorous character of the cluster expansion vindicates the seemingly phenomenological Ising model as a fundamentally correct representation of the energy of partially ordered alloys, i.e. alloys displaying both short- and/or long-range order. In this representation, the alloy Hamiltonian includes many-body terms as well as temperature and volume dependence. Issues that remain to be fully explored, however, are the range of interactions and local elastic distortions. Nevertheless, neglecting local elastic relaxations and assuming a relatively short range of interactions, configurational free energies can be easily calculated using the CVM and, from them, the solid state portion of phase diagrams.

The success of the cluster representation for the energy of alloys led Connolly and Williams17) to propose the use ab-initio total energy calculations of ordered compounds, in lieu of experimental data, as a mean of obtaining the set of effective pair and multisite chemical interactions. Although an extension of the phenomenological approach, the proposal of Connolly and Williams reflected the degree of confidence with which total energies could be calculated using the local-density approximation, and opened the door to first principles calculation of phase diagrams.

Among the first applications of this first-principles approach were studies of temperature-composition binary phase diagrams of noble-metal alloys18) and of semiconductor alloys.19) Subsequently, numerous other cases have been investigated with relativily good results20)~27) including ternary phase equilibrium.28)

In general, and neglecting elastic relaxations, the implementation of the cluster expansion method for any particular system requires detailed consideration of three important aspects. First is the convergence of the interactions in the cluster expansion of the Hamiltonian which, in general, cannot be ascertained a-priori. Several of the studies mentioned above have addressed this subject and established criteria for judging convergence. In particular, a converged expansion, obtained from one set of ordered structures, should accurately reproduce the total energies of structures outside this set. Studies that include only nearest-neighbors or second-nearest neighbors interaction range may have to be re-examined with this aspect in mind. Second the range of interaction in the Hamiltonian must be self-consistent with the statistical approximation of the CVM. Calculations using well-converged cluster expansions of the Hamiltonian, but that rely on small cluster approximations, should also be subject to close re-examination. Finally, vibrational modes are expected to contribute significantly to the total free energy and, therefore, they should be incorporated in any predictive theory of alloy phase equilibrium. Most first-principles phase diagram calculations to date have discounted or neglected vibrational effects or have incorporated vibrational entropy using strictly empirical means.

Here, first-principles electronic structure calculations are used to study phase equilibrium in the zirconium-niobium system. This study incorporates the bcc to hcp structural transition in Zr-rich alloys, that is driven by the vibrational free energy, as well as phase separation that is determined, primarily, by the configurational free energy. The emphasis is placed on the development of a predictive ab-initio theory of alloy phase stability that incorporates electronic structure, configurational entropy and vibrational modes. It is shown that a computationally tractable and accurate theory can be achieved by addressing each of the three aforementioned aspects of the method. In particular, for the zirconium-niobium system, the cluster expansions of the energy is shown to be well converged, the CVM is implemented self-consistently with respect to the interactions included in the Hamiltonian, and vibrational modes are incorporated in the Debye-Grüneisen approximation. The result, as we shall see, is excellent agreement with experiment.

In the next section we review the cluster algebra used in description of the configurational thermodynamic of alloys. The theory provides the formal framework for the treatment of short-range order (SRO) effects in the configurational energy and is very close in spirit to Kikuchi's method for the configurational entropy. The contribution to the free energy due the vibrational modes is also discussed. We make contact with microscopic electronic theories via the Linear Muffin-Tin Orbital (LMTO) approximation, which is used to calculate the total energies of selected compounds in the Zr-Nb system.

§ 2. Configurational thermodynamics

In this section we review a general formalism for a cluster description of the configurational thermodynamics of alloys. The main result is that functions of configuration can be described, quite generally, by means of a cluster expansion. As pointed out in the Introduction, this expansion suggests that the energy of disordered alloys may be conveniently characterized from the knowledge of the energy (binding curves) of few ordered compounds. For the sake of simplicity we consider only binary systems although the theory can be easily extended to multicomponent alloys.[16)]

2.1. *Cluster expansion*

As usual, the configuration of a crystalline binary alloy is described in terms of occupation numbers σ_i at each lattice site i. For a binary alloy, the occupation numbers take values $+1$ and -1 for components A and B, respectively. Each of the 2^N configurations of the binary alloy is then given by the N-dimensional vector $\boldsymbol{\sigma}=\{\sigma_1, \sigma_2 \cdots, \sigma_N\}$, where N is the number of lattice points. In general, we want to address the problem of describing functions that depend explicitly on the occupation variables σ_i, such as the energy of alloy formation. An unambiguous description of such functions is obtained by introducing an orthogonal and complete functional basis in configurational space. In the thermodynamic limit, the dimension of this complete orthogonal basis is infinite. However, it is usually found that a judicious choice of a finite set of basis functions is sufficient to approximate most physical properties in real systems.

In order to construct the orthogonal basis set we begin by defining two orthogonal polynomials in the discrete variable σ_i at a given single site i: the polynomial of order 0, $\phi_0(\sigma_i)=1$, and the polynomial of order 1, $\phi_1(\sigma_i)=\sigma_i$. In the one-dimensional discrete space spanned by σ_i, these polynomials form a complete and orthonormal set, with the inner product between two functions of configuration, $f(\sigma_i)$ and $g(\sigma_i)$, defined as,[16)]

$$\langle f(\sigma_i)\cdot g(\sigma_i)\rangle=\frac{1}{2}\sum_{\sigma_i=\pm1} f(\sigma_i)g(\sigma_i)\,. \tag{1}$$

The set of orthonormal characteristic functions in the N-dimensional discrete space spanned by the vector $\boldsymbol{\sigma}$ is obtained from the direct product of the $\{\phi_0(\sigma_i), \phi_1(\sigma_i)\}$, where i spans all crystal sites ($i=1, 2, \cdots N$). For a binary system, the resulting characteristic functions, $\Phi_\alpha(\boldsymbol{\sigma})$, are given by products of the spin operator σ_i over the sites of all possible clusters $\alpha=\{i_1, i_2, \cdots i_n\}$ in the crystal:[16)]

$$\Phi_\alpha(\boldsymbol{\sigma})=\prod_{i\in\alpha}\sigma_i=\sigma_{i_1}\sigma_{i_2}\cdots\sigma_{i_n}\,. \tag{2}$$

Accordingly, there is a one to one correspondence between the set of orthogonal functions $\Phi_\alpha(\boldsymbol{\sigma})$ and the set of all clusters α in the crystal, including the empty cluster for which $\Phi_0(\boldsymbol{\sigma})=1$.

Orthogonality of the characteristic functions $\Phi_\alpha(\boldsymbol{\sigma})$ is expressed by:[16)]

$$\frac{1}{2^N}\sum_{\boldsymbol{\sigma}}\Phi_\alpha(\boldsymbol{\sigma})\Phi_\beta(\boldsymbol{\sigma})=\delta_{\alpha,\beta} \tag{3a}$$

and completeness by:

$$\frac{1}{2^N}\sum_{\alpha}\Phi_\alpha(\boldsymbol{\sigma})\Phi_\alpha(\boldsymbol{\sigma}')=\delta_{\sigma,\sigma'}\,. \tag{3b}$$

If follows from Eqs. (3) that any function of configuration, $F(\boldsymbol{\sigma})$, may be written as

$$F(\boldsymbol{\sigma})=\sum_{\alpha} F_{\alpha}\Phi_{\alpha}(\boldsymbol{\sigma})\,, \tag{4}$$

where the sum extends over all clusters in the crystal, including the empty cluster, and where the projections of $F(\boldsymbol{\sigma})$ on the orthogonal cluster basis, F_{α}, are given by,

$$F_{\alpha}=\langle F(\boldsymbol{\sigma})\cdot\Phi_{\alpha}(\boldsymbol{\sigma})\rangle=\frac{1}{2^N}\sum_{\boldsymbol{\sigma}} F(\boldsymbol{\sigma})\Phi_{\alpha}(\boldsymbol{\sigma})\,. \tag{5}$$

In general, Eq. (4) may be simplified by noting that the space group symmetry of the crystal requires that the cluster projection F_{α} be the same for all clusters α related by a symmetry operation (translation or point group). Accordingly, the cluster expansion in Eq. (4) becomes:

$$F(\boldsymbol{\sigma})=\sum_{n} F_{n}\Theta_{n}(\boldsymbol{\sigma})\,, \tag{6}$$

where n labels the set of inequivalent clusters in the crystal. In the case of a disordered lattice, these clusters are distinguished by their number of points and their geometry. In Eq. (6), the $\Theta_n(\boldsymbol{\sigma})$ are given by:

$$\Theta_{n}(\boldsymbol{\sigma})=\sum_{\alpha\in n} \Phi_{\alpha}(\boldsymbol{\sigma})\,. \tag{7}$$

In view of the orthogonality of the $\Phi_{\alpha}(\boldsymbol{\sigma})$, we also have:

$$\frac{1}{2^N}\sum_{\boldsymbol{\sigma}} \Theta_{n}(\boldsymbol{\sigma})\Theta_{m}(\boldsymbol{\sigma})=z_n N\delta_{n,m}\,, \tag{8}$$

where $z_n N$ is the total number of n-type clusters in the crystal.

The cluster expansion, Eq. (6), takes a particularly useful form when applied to the probability of configuration $\boldsymbol{\sigma}$, $X(\boldsymbol{\sigma})$:

$$X(\boldsymbol{\sigma})=\frac{1}{2^N}[1+\sum_{n>0}\Theta_{n}(\boldsymbol{\sigma})\xi_n]\,, \tag{9}$$

where the term in the expansion for the empty cluster was singled out and, thus, the sum over the characteristic functions exclude the empty cluster. The ξ_n are the correlation functions which, in view of Eq. (5), are also the expectation values of the characteristic functions:

$$\xi_n=2^N\langle X(\boldsymbol{\sigma})\cdot\Phi_{\alpha}(\boldsymbol{\sigma})\rangle=\sum_{\boldsymbol{\sigma}} X(\boldsymbol{\sigma})\Phi_{\alpha}(\boldsymbol{\sigma})=\langle\Phi_{\alpha}(\boldsymbol{\sigma})\rangle\,, \tag{10}$$

where α is any cluster belonging to the equivalent set n.

Combining Eqs. (6), (7) and (10), it follows that expectation values of functions of configurations, such as the average of the configurational energy, can be quite generally written in the form:

$$\bar{F}=\langle F(\boldsymbol{\sigma})\rangle=N\sum_{n} z_n F_n\xi_n\,. \tag{11}$$

The cluster algebra developed in this section, and in particular the cluster expansion, provides formal justification to the many recent applications of the Connolly-Williams approach to the characterization of the configurational energies from first principles electronic structure calculations. An example of the use of this formalism will be given in § 3 for the Zr-Nb system.

2.2. *The effective interactions*

The cluster expansion of the energy applied to a set of ordered compounds allow us, in general, to define a set of effective chemical interactions by direct inversion of Eq. (11). The procedure requires assumptions concerning the dominant interactions, which are to be included in the cluster expansion, as well as the knowledge of the energies and the correlation functions for an invertible set of ordered compounds. In what follows, we will assume that the energy of the compounds are known. In general they include the electronic binding energy $E(\Omega)$, function of the volume Ω, and temperature dependent contributions arising from the vibrational modes. We will return to the computation of the electronic binding energy in § 3. The vibrational free energy for each compound will be approximated using the Debye-Grüneisen model. Thus, the general form of the energy is[27),28)]

$$F(\Omega,\ T)=\frac{9}{8}k_B\Theta+E(\Omega)-k_B T[D(\Theta/T)-3\ln(1-\exp(-\Theta/T))]\,, \tag{12}$$

where k_B is Boltzmann's constant, $D(x)$ is the Debye function, $E(\Omega)$ is the electronic binding energy, and where the volume dependence of the Debye temperature, Θ_k, is given by:

$$\Theta=\Theta_0(\Omega_0/\Omega)^{\gamma} \tag{13}$$

with Θ_0 the Debye temperature corresponding to Ω_0, and with γ the Grüneisen constant.

For ordered compounds, the free energy given by Eq. (12) represents the volume and temperature dependent binding energy in the absence of configurational disorder. Defining the correlation functions $\xi_n^{(k)}$ —where $k=1, 2, \cdots m$ labels a set of m ordered compounds and n labels the interactions included in the cluster expansion — the vibrational free energy (per atom) for each of the ordered structures, $F_k(\Omega,\ T)$, takes the form:

$$F_k(\Omega,\ T)=\sum_{n=0}^{m} z_n V_n(\Omega,\ T)\xi_n^{(k)}\,, \tag{14}$$

where the coefficients $V_n(\Omega,\ T)$ are volume and temperature dependent effective interactions.

At a fixed volume and temperature, inversion of Eq. (14) yields:

$$V_n(\Omega,\ T)=\sum_{k=0}^{m}\omega_k^{(n)}F_k(\Omega,\ T)\,, \tag{15}$$

where the coefficients ${\omega_k}^{(n)}$ are obtained by inversion of the matrix with elements $z_n{\xi_n}^{(k)}$.

Note that volume relaxation is to be incorporated globally by minimizing the free energy functional with respect to Ω, in addition to the usual minimization with respect to the correlation functions ξ_n. This global volume relaxation plays an important role in alloy formation. It should be emphasized, however, that local elastic relaxations, which are expected to be present in disordered alloys, are not included in the present treatment.

2.3. *Configurational entropy*

Since the introduction of the CVM in 1951 by Kikuchi,[1)] the method has been reformulated using a number of different points of view. Here, we briefly review the derivation of the CVM based on an exact Möbius transformation and a strictly algebraic approach.[16)] This particular derivation clearly shows the CVM to be a generalization of the mean-field ideas that have been so successfully used in statistical mechanics.

We begin by introducing the probability distribution for cluster α, $X_\alpha(\boldsymbol{\sigma}_\alpha)$, which is given by the sum of the $X(\boldsymbol{\sigma})$ over all configurational variables σ_i outside cluster α. Here, $\boldsymbol{\sigma}_\alpha$ stands for the vector of occupation numbers in cluster α. The probability distribution allows to define effective cluster Hamiltonians, $H_\alpha(\boldsymbol{\sigma}_\alpha)$, through the relation:

$$X_\alpha(\boldsymbol{\sigma}_\alpha)=\exp(-H_\alpha(\boldsymbol{\sigma}_\alpha)/kT)\,. \tag{16}$$

The cluster Hamiltonians include, in addition to the bare interactions in each cluster, the mean field effect of the lattice. As shown in § 2.1, the $H_\alpha(\boldsymbol{\sigma}_\alpha)$ can be written in terms of the characteristic functions associated to cluster α. The most general form for $H_\alpha(\boldsymbol{\sigma}_\alpha)$ is:

$$H_\alpha(\boldsymbol{\sigma}_\alpha)=kT\ln Z_\alpha+\sum_{\beta\in\alpha}{}' h_\beta^{(\alpha)}\Phi_\beta(\boldsymbol{\sigma}_\beta)\,, \tag{17}$$

where the prime in the sum indicates the term corresponding to the empty cluster, which has been singled out as $kT \ln Z_\alpha$, is excluded. The effective interactions $h_\beta^{(\alpha)}$ are the projections of the cluster Hamiltonians on the orthogonal basis according to Eq. (5).

The fundamental problem is to relate the cluster Hamiltonians $H_\alpha(\boldsymbol{\sigma}_\alpha)$ to that of the whole crystal:

$$H(\boldsymbol{\sigma})=kT\ln Z+\sum_\beta{}' V_\beta\Phi_\beta(\boldsymbol{\sigma}_\beta)\,, \tag{18}$$

where Z is the usual partition function and the V_β are the bare interactions introduced in § 2.2. The relationship in question can be established through an exact Möbius transformation. This transformation defines *irreducible* cluster Hamiltonians, $\hat{H}_\alpha$, through relations of the form:[16)]

$$H_\alpha(\boldsymbol{\sigma}_\alpha)=\sum_{\alpha\supseteq\beta}\hat{H}_\beta(\boldsymbol{\sigma}_\beta)\,, \tag{19}$$

where the sum runs over all the subclusters β of α, including α. Equivalently, the crystal Hamiltonian is given by

$$H(\boldsymbol{\sigma})=\sum_{\beta}{}'\hat{H}_{\beta}(\boldsymbol{\sigma}_{\beta})\,, \tag{20}$$

where the sum runs over all clusters in the crystal.

The key approximation made in the CVM is that of neglecting the irreducible energy contributions $\hat{H}_{\alpha}$ for clusters larger than a given maximum cluster. This closure condition allows us to express the crystal Hamiltonian H in terms of sum of irreducible contributions over a subset of clusters that, once symmetry is considered, is finite. Furthermore, since there is a linear relation between the effective and the irreducible cluster Hamiltonians, we may express Eq. (20) as:

$$H(\boldsymbol{\sigma})=\sum_{\alpha}{}''a_{\alpha}H_{\alpha}(\boldsymbol{\sigma}_{\alpha})\,, \tag{21}$$

where the sum runs over all clusters in the crystal contained in the set of maximum clusters. The coefficients a_{α} are given by

$$\sum_{\beta\supseteq\alpha}{}''a_{\beta}=1\,, \tag{22}$$

where the equation is valid for each subcluster α of the maximum cluster, and where the sum runs over all subclusters β of the maximum clusters that contain or equal α. In general, the computation of the a_{β} and, particularly, the bookkeeping of cluster probabilities are somewhat tedious for large clusters and/or lattices of low symmetry. However, using simple group theoretical arguments the procedure can be easily programmed in a computer.

Equation (21) is the fundamental CVM relation for the mean-field Hamiltonians $H_{\alpha}(\boldsymbol{\sigma}_{\alpha})$. The equation may be cast in the form of a set of algebraic nonlinear equations by projecting onto the basis of orthogonal characteristic functions $\Phi_{\alpha}(\boldsymbol{\sigma}_{\alpha})$:

$$\langle H(\boldsymbol{\sigma})\cdot\Phi_{\alpha}(\boldsymbol{\sigma}_{\alpha})\rangle=\sum_{\alpha}{}''a_{\alpha}\langle H_{\alpha}(\boldsymbol{\sigma}_{\alpha})\cdot\Phi_{\alpha}(\boldsymbol{\sigma}_{\alpha})\rangle\,, \tag{23}$$

which, for the empty cluster, gives

$$kT\ln Z=\sum_{\alpha}{}''a_{\alpha}\ln Z_{\alpha} \tag{24}$$

and, for the other clusters included in the approximation:

$$V_{\alpha}=\sum_{\beta}{}''a_{\beta}h_{\alpha}{}^{(\beta)}\,. \tag{25}$$

Equation (25), derived here following a generalized mean-field approach, correspond to the usual minimization conditions of the CVM whereas Eq. (24) gives the CVM equilibrium free energy.

A point of some practical interest is that the algebra developed in § 2.1 is of course applicable to finite clusters. Thus, introducing symmetry and the notation established in § 2.1, the cluster probabilities are given by

$$X_{n}(\boldsymbol{\sigma}_{n})=\frac{1}{2^{n}}[1+\sum_{m\le n}\Theta_{m}{}^{(n)}(\boldsymbol{\sigma}_{n})\xi_{m}] \tag{26}$$

with the $\Theta_{m}{}^{(n)}(\boldsymbol{\sigma}_{m})$ now given by

$$\Theta_m^{(n)}(\sigma_n)=\sum_{\alpha\in m}{}''\Phi_\alpha(\sigma_\alpha)\,. \tag{27}$$

Here the sum is restricted to all clusters α of type m that are contained in a *given* cluster β of type n. These relations follow by straightforward application of Eqs. (7) and (9) to a finite cluster n.

Furthermore, imposing the crystal symmetry to the mean-field cluster interactions $h_\alpha^{(\beta)}$, and with the help of Eqs. (16), (17) and (27), the self-consistency relations, Eq. (25), can also be written as

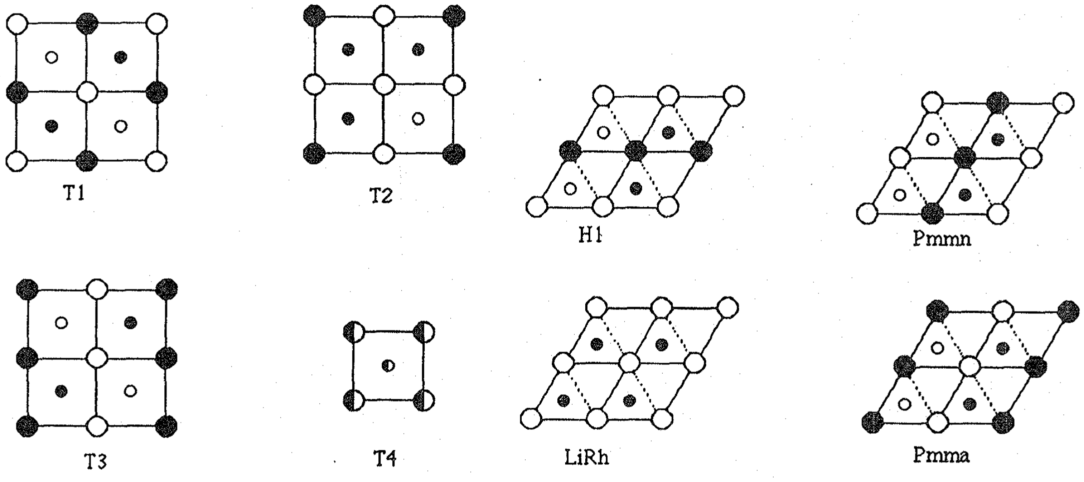
$$z_n V_n=-kT\sum_{m\geq n} z_m a_m \frac{1}{2^m}\sum_{\sigma_m}\Theta_n^{(m)}(\sigma_m)\ln X_m(\sigma_m)\,. \tag{28}$$

Thus, in order to solve Eq. (28) numerically, it is convenient to use the correlation functions ξ_n as the set of independent variables. In many instances this choice facilitates the use of efficient methods for solving nonlinear equations, such as the Newton-Raphson algorithm, since the Jacobean of the system can be calculated in a straightforward manner.

§ 3. The Zr-Nb system

The total energies as a function of atomic volume of seven hcp and ten bcc lattice structures were calculated for different compounds of the form Zr_xNb_{1-x}. As mentioned, these calculations use only atomic numbers and atom positions as input and are expected to correctly reproduce 0 K ground state properties.

The bcc-based structures investigated include the pure elements with the tungsten structure (bcc), the Zr_3Nb and $ZrNb_3$ compounds with the DO_3 structure, and ZrNb with the B2 and the B32 structures. Total energies were also calculated for four simple tetragonal structures, with stoichiometry ZrNb and ratio $c/a=0.5$. Projected unit cells for these tetragonal structures, labeled T_i, with $i=1$ to 4, are shown in Fig. 1(a). The following hcp-based compounds, with ideal c/a ratio, were calculated: the



(a) (b)

Fig. 1. Structures with stoichiometry ZrNb for which the total energies were calculated. (a) bcc-based compounds; (b) hcp-based compounds.

Table I. Correlation functions for compounds based on the bcc structure. The last row indicates the coordination numbers z_n for each cluster.

Structure	Empty	Point	Pair	Pair(2nd)	Pair(3rd)	Triang.	Tetra.
bcc(A)	1	1	1	1	1	1	1
DO_3(A3B)	1	1/2	0	0	1	−1/2	−1
B2(AB)	1	0	−1	1	1	0	1
B32(AB)	1	0	0	−1	1	0	1
DO_3(AB3)	1	−1/2	0	0	1	1/2	−1
bcc(B)	1	−1	1	1	1	−1	1
T1(AB)	1	0	0	−1/3	−1/3	0	−1/3
T2(AB)	1	0	−1/4	1/3	0	0	0
T3(AB)	1	0	0	0	−1/3	0	−1/3
T4(AB)	1	0	0	1/3	−1/3	0	−1/3
z_n	1	1	4	3	6	12	6

Table II. Correlation functions for compounds based on the hcp structure. The last row indicates the coordination numbers z_n for each cluster.

Structure	Empty	Point	Pair	Pair(2nd)	Triang.	Tetra.
hcp(A)	1	1	1	1	1	1
DO_{19}(A3B)	1	1/2	0	1	−1/2	−1
Pmma(AB)	1	0	−1/3	1	0	1
Pmmn(AB)	1	0	0	−1	0	−1
DO_{19}(AB3)	1	−1/2	0	1	1/2	−1
hcp(B)	1	−1	1	1	−1	1
LiRh(AB)	1	0	0	−1	0	−1
H1(AB)	1	0	−1/6	0	0	0
z_n	1	1	6	3	8	2

pure elements with the hcp structure the Zr_3Nb and $ZrNb_3$ with the DO_{19} structure, and ZrNb with the LiRh, *Pmmn* and *Pmma* structures, plus an additional structure labeled H1. The projected unit cells for the all the ZrNb compounds based on the hcp structure are shown in Fig. 1(b).

The correlation functions $\xi_n^{(k)}$ and the coordination numbers z_n for selected clusters are shown in Table I for the bcc and in Table II for the hcp-based structures. In both cases, the clusters included in Tables I and II are: the empty cluster, the point cluster, first- and second-neighbor pairs, and the triangle and tetrahedron clusters. For the bcc structures, third-neighbor pairs are also included.

3.1. *Electronic structure calculations*

The total energies were calculated in the local-density approximation, with the electronic structure in each case determined using the linear muffin-tin orbital method[30] in the atomic sphere approximation (LMTO-ASA) with combined correction terms. This approximation renders the total energies correct to first order.[30] The Hedin-Lundquist exchange-correlation potential was used,[31] and spin-orbit coupling was not included.

For phase diagram computations, a relative accuracy for the energy of formation of the different compounds of the order or better than 1 mRy is usually required. Thus, the numerical accuracy, particularly when comparing compounds calculated with different structure matrices, needs to be ascertained carefully. For all structures, the convergence of the Ewald sum for the structure matrix was assured by increasing the number of vectors (both in real and $\boldsymbol{k}$-space) until a doubling of the number of vectors produced a change in the resulting total energy of no more than 0.1 mRy per atom. The mesh density in $\boldsymbol{k}$-space was tested similarly. For bcc structures, a mesh of 650 k-points in the irreducible wedge of the Brillouin zone was used.

The calculated total energy binding curves for the pure elements and compounds are accurately described by a Morse function of the form:[29)]

$$E(\Omega)=A-2Ce^{-\lambda(r-r_0)}+Ce^{-2\lambda(r-r_0)}, \tag{29}$$

where $E(\Omega)$ is the calculated electronic binding energy of the rigid lattice and A, C, λ, and r_0 are fitting parameters. Here, the variable r is the Wigner-Seitz atomic radius related to the volume per atom by the relation $\Omega=(4\pi/3)r^3$. For the compounds, r is the *effective* Wigner-Seitz radius obtained from the average of the constituent atomic volumes. It follows from Eq. (29) that r_0 is the Wigner-Seitz radius corresponding to the minimum in the binding curve and that C is the cohesive energy of the rigid lattice.

In order to include the vibrational modes, as discussed in § 2.2, an estimate of the Debye temperature and the Grüneisen constant is needed for each compound. For cubic metals, Moruzzi et al.[29] have shown that accurate estimates of Debye temperatures can be obtained directly from the calculated electronic binding energies by assuming isotropic longitudinal and transverse sound velocities, a Poisson's ratio

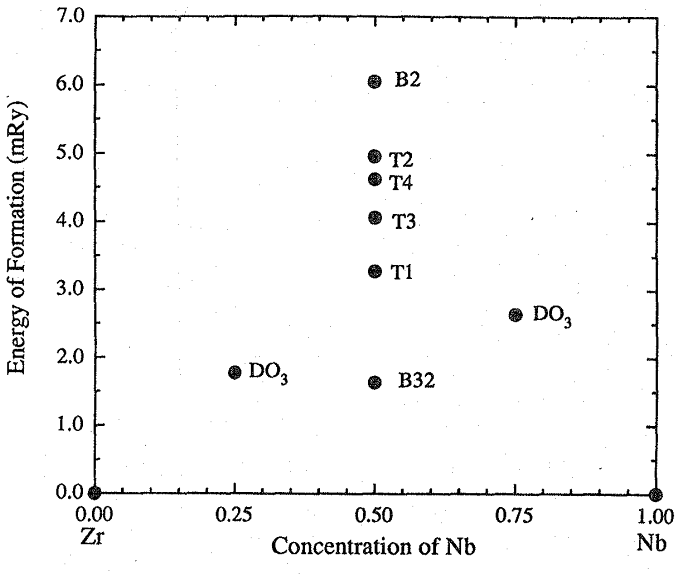


Fig. 2. Ground state diagram for bcc-based compounds in the Zr-Nb system.

approximately equal to 1/3, and a ratio of shear to bulk modulus of 0.3. As shown by Moruzzi et al.,[29] these assumptions are supported by experiment. The relation for the Debye temperature at the equilibrium volume is:

$$\Theta_0 = G_C \left[\frac{r_0 B}{M} \right]^{1/2} \tag{30}$$

with the proportionality constant $G_C = 41.63$ K sec for cubic systems.

The assumptions above are, in general, not applicable to hexagonal metals as there are five independent elastic constants and a more pronounced anisotropy. For simplicity we also adopted Eq. (30) for the hcp systems, but with a numerical constant $G_h = 45.95$ K sec. This numerical coefficient was chosen in order to reproduce the $\alpha \to \beta$ (hcp→bcc) transition temperature of 1193 K observed in pure Zr. We note that with this choice of G_h the Debye temperature of hcp Zr turns out to be 300.75 K, in close agreement to the experimental value of 291 K.

The results of the electronic structure calculations, in the form of the Morse parameters and the Debye and Grüneisen constants, are summarized, respectively, in Tables III and IV, for all the bcc, except structure T4, and the hcp compounds

Table III. Morse parameters, Debye temperature and Grüneisen constant for bcc-based compounds.

Compound	r_0[au]	λ[au^{-1}]	D[Ry]	A[Ry]	Θ_0[K]	γ
Zr(bcc)	3.40	0.83	0.699	0.701	269	1.42
Nb(bcc)	3.17	1.04	0.743	0.743	409	1.65
$Zr_3Nb(DO_3)$	3.34	0.87	0.720	0.724	284	1.46
ZrNb(B2)	3.28	0.93	0.717	0.724	301	1.53
ZrNb(B32)	3.28	0.94	0.719	0.722	304	1.53
ZrNb(T1)	3.28	0.94	0.713	0.718	303	1.54
ZrNb(T4)	3.28	0.93	0.716	0.722	302	1.53
ZrNb(T5)	3.28	0.93	0.715	0.720	302	1.53
$ZrNb_3(DO_3)$	3.22	0.99	0.731	0.734	323	1.59

Table IV. Morse parameters, Debye temperature and Grüneisen constant for hcp-based compounds.

Compound	r_0[au]	λ[au^{-1}]	D[Ry]	A[Ry]	Θ_0[K]	γ
Zr(hcp)	3.42	0.86	0.689	0.689	301	1.46
Nb(hcp)	3.19	1.04	0.722	0.748	370	1.65
$Zr_3Nb(DO_{19})$	3.36	0.88	0.706	0.717	314	1.49
ZrNb(*Pmma*)	3.30	0.94	0.702	0.722	330	1.55
ZrNb(*Pmmn*)	3.30	0.94	0.696	0.715	331	1.55
ZrNb(H1)	3.30	0.94	0.700	0.720	330	1.55
ZrNb(LiRh)	3.30	0.94	0.694	0.714	330	1.56
$ZrNb_3(DO_{19})$	3.25	0.99	0.708	0.733	350	1.60

investigated. A ground state diagram indicating the energy of formation for the bcc based compounds at their equilibrium volumes is shown in Fig. 2.

The convergence of the cluster expansion for the bcc structure was ascertained by comparing ground-state energies obtained from electronic structure calculations for compounds outside of the basis set, with energies predicted by the cluster expansion itself. Using a basis set of six compounds, that includes the pure elements, the DO_3, B2 and B32 structures, allows a cluster expansion up to second-nearest neighbors (including three- and four-body terms). The basis was also augmented with a simple tetragonal structure, T1, in order to include third-nearest neighbors pair interactions. The results are shown in Table V, where the LMTO energy of formation for each of the compounds outside the basis set is given (second columns), together with the difference between this energy and that predicted by the cluster expansion. The comparison is done for the expansions carried out up to second (column labeled Second) and up to third neighbor interactions (columns labeled Third). For the expansion including third neighbors, the errors for each of three possible basis sets are shown. The inclusion of third-nearest neighbors yields a slight improvement in the compound energy for the additional tetragonal structures, T2, T3 and T4.

The finite temperature free energy calculations were performed using the CVM in the tetrahedron-octahedron approximation for the hcp alloys, which is consistent with the second-nearest neighbor interactions included in the Hamiltonian. For the bcc structures, the maximum clusters used were the bcc octahedron plus the nine points bcc unit cell, which explicitly include up to the third-nearest neighbor pairs. Thus, the CVM approximations for both the bcc and hcp structures are consistent with the range of interactions assumed in the cluster expansion for the energy.

The resulting phase diagram is shown in Fig. 3 along with experimental data from Flewitt,[32] Lundin and Cox,[33] Roger and Adkins,[34] and Abriata and

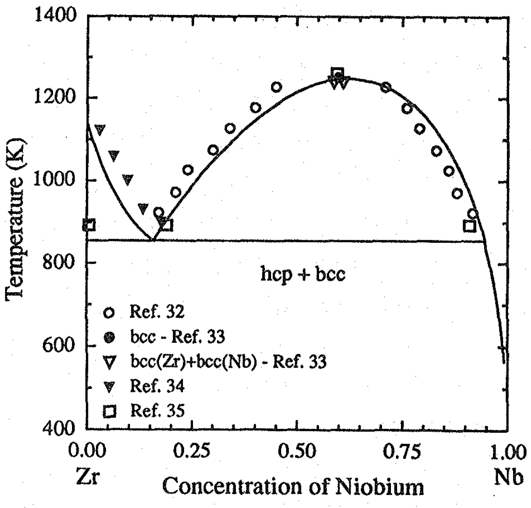


Fig. 3. Calculated phase diagram for Zr-Nb compared with experimental data.

Table V. Energies of formation for the four tetragonal structures from the LMTO calculations and the associated errors obtained from the cluster expansions.

Structure	E[mRy] (LMTO)	Error in cluster expansion [mRy]			
		Second	Third		
ZrNb(T1)	3.3	0.15	0.00	−0.37	−0.15
ZrNb(T2)	4.6	0.39	0.28	0.00	0.17
ZrNb(T3)	4.1	0.30	0.15	−0.22	0.00
ZrNb(T4)	5.0	1.23	1.09	0.71	0.93

Bolcich.[35] The top of the predicted miscibility gap is at 1248 K and a concentration of 62% Nb, 1.3% below the measured 1261 K at 61% Nb. As mentioned, the relationship between bulk modulus and the Debye temperature for the hexagonal structures was adjusted to reproduce the α(hcp) → β(bcc) transition of pure Zr. We emphasize, however, that this ad-hoc adjustment gives a Debye temperature (300.75 K) that is approximately 3% higher than the experimental value (291 K). With the adjusted Debye temperature, the predicted monotectoid equilibrium temperature (855 K) is within 6.5% of the measured temperature (893 K).

§ 4. Conclusions

The fundamental theoretical background needed for the first-principles calculation of phase diagrams was briefly reviewed and applied to the Zr-Nb system. The method involves the characterization of the electronic structure of ordered compounds, an expansion of the energy in terms of multisite characteristic functions (or correlation functions), the use of the CVM to calculate configurational free energies, and the implementation of the Debye-Grüneisen approximation for treatment of the vibrational modes. It was shown that excellent agreement with experiment can be achieved, provided a converged cluster expansion and a consistent CVM approximation are used. The issue of vibrational free energies was also investigated. It was shown that a semi-empirical estimate, in lieu of first principles phonon spectrum calculations, can be obtained following the approach proposed by Moruzzi et al.[29] In the case of Zr-Nb this latter contribution is crucial since it determines the α(hcp) → β(bcc) transition in Zr-rich alloys. For the Zr-Nb system it was also shown that a sufficiently accurate description of the miscibility gap can be accomplished using ab-initio methods without adjustable parameters. The amount of computational work is not excessive in this system, although one should expect that, for other systems where interactions are of longer range, numerical and practical complications may arise.

The CVM has played a prominent role in both phenomenological and first principles calculations of phase diagrams, not only by providing an efficient way of computing configurational entropies but also by the establishing a systematic description of short range order in alloys which, ultimately, led to the development of a cluster expansion for the energy and to the Connolly-Williams method. Thus, although much work remains to be done, it appears that we are on the way to a truly predictive first-principles theory of alloy phase stability. Among the problems that are likely to be the focus of future work are the effect of elastic relaxations and applications to multicomponent systems.

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