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ABSTRACT

Many stable or metastable intermetallic phases useful to the alloy designer have crystal structures which are ordered superstructures of a parent disordered phase. A highly reliable statistical mechanical method (CVM) has now been developed for calculating such superstructure phase equilibria derived from say, the fcc parent lattice. To obtain phase diagrams, one needs certain physical parameters, such as effective pair interaction ratios. It is possible, in principle, to extract these parameters from band structure calculations in the coherent potential approximation (CPA), particularly from recently developed cluster-CPA techniques. If sufficient accuracy can be achieved

1. INTRODUCTION

As explained elsewhere in these conference proceedings, particular ordered structures are found to produce excellent mechanical properties in certain classes of alloys. The alloy designer would of course like to predict what sorts of alloying elements and heat treatments will promote which structures. If we restrict attention to superstructures of a given parent lattice, say the $L1_2$ structure in fcc, the problem appears to be amenable to theoretical solution. In other words, it may be possible, in favorable cases, to predict what ordered phases will be stable (or at least metastable) under what conditions, by performing purely first-principles calculations, i.e., ideally, from a knowledge of the atomic numbers of the elements considered, the temperature and the average composition.

The purpose of this paper is to summarize recent results which presently lead one to believe that such first-principles calculations may soon become quite feasible. Both band structure and configurational entropy aspects will be briefly covered. Possible experimental techniques which are available for verification of the theoretical predictions will be mentioned.

The present treatment will be essentially qualitative. For more detailed accounts, the reader is referred to the cited references. Background can be found, for example, in the author's early review paper [1].

2. STATE OF ORDER

In general, crystalline alloy phases are **disordered systems**. If we disregard, for simplicity, small atomic displacements from lattice sites, the disorder is essentially **compositional**. Perfect stoichiometric compounds (complete order) and completely disordered solid solutions (complete disorder) are extreme special cases of the general one under consideration here: that of **partial order**.

How does one describe such states? Perfect order is completely described by specifying the crystallographic unit cell. Total disorder is completely described by the average concentration since, by definition, the occupation probability of each lattice point is the same, namely the average concentration c ($\equiv x_B$ of B, say, in an A-B alloy), independently of the environment, since all correlations vanish. Hence, one may state that the unit cell is the appropriate descriptive unit for complete order, and the lattice point (occupied by an "average atom") is the appropriate one for complete disorder.

For partial order (or disorder), the appropriate descriptive unit is the cluster of lattice points. If the cluster is the whole crystal, we obtain an exact but impractical description of the state of order. Hence, only small clusters are retained, the smallest one, beyond the point, being the pair (1st, 2nd, 3rd...neighbors). One can also envisage triplets of lattice point, quadruplets (tetrahedra,...), etc. States of order can then be described by a so-called "cluster algebra" [2] which makes use of multiplet correlation functions ξ defined as follows:

$$\xi_{m,s} = \langle \sigma_1 \sigma_2 ... \sigma_m \rangle \tag{1}$$

for a cluster of m lattice points, the subscript denoting the site in the cluster. In Eq.(1), the σ are occupation variables taking value +1 or -1 depending on the occupation of the site, A or B. The brackets indicate an

average of the σ product over the whole crystal, or better, over an ensemble of systems, and the index s labels the type of m-point cluster.

A cluster (of n points, of type r, say) may be populated by A and B atoms in a certain way, i.e., it may have a certain configuration (J), with resulting frequency of occurrence, or probability, or cluster concentration x given by [2,3]

$$x_{n,r}(J) = \frac{1}{2^n} [1 + \sum_{m,s} \nu_{n,r;m,s}(J) \, \xi_{m,s}] \tag{2}$$

where the (rectangular) matrix ν has elements given by sums of products of plus ones and minus ones. The nature of the ν-matrix is entirely fixed by the nature of the crystal lattice and by the largest clusters (and their sub-clusters) used. The multiplet correlations ξ form a set of linearly independent variables which completely describe the state of order at the level of approximation desired. These variables are thus the fundamental ones not only for the problem at hand, but also for calculating the internal energy, determining the ordered ground states and for calculating the configurational free energy of the system at arbitrary temperature, as will be seen in Sects. 3, 4 and 5.

3. INTERNAL ENERGY

It was stated above that a complete and exact description of the state of order could be given by specifying the statistical weights X(J) of all possible configurations J of the whole crystal, J denoting a given distribution of +1 and -1 over the $N = N_A + N_B$ points of the crystal, N_A and N_B being the fixed number of A and B atoms in the crystal. Let configuration J have energy E(J). For fixed concentration, the expectation value of the energy is then given by a canonical ensemble average over all $M = N!/(N_A!N_B!)$ configurations J_0 having concentration $c = N_B/N$:

$$\langle E \rangle = \sum_{J_0} X(J_0) \, E(J_0), \tag{3}$$

This expression is exact; it can be written in terms of independent variables ξ by means of Eq. (2) applied to X, the "cluster concentration" of the whole crystal [3,4]. Upon substitution of Eq. (2), written for the whole crystal, into (3), one finds, after subtracting the energy of the completely disordered state:

$$\langle E \rangle = E_0 + \sum_{m,s} \epsilon_{m,s} \, \delta\xi_{m,s} \tag{4}$$

in which

$$E_0 = \frac{1}{M} \sum_{J_0} E(J_0) \tag{5}$$

is the energy of the disordered state of composition c, and where $\delta\xi_{m,s} = \xi_{m,s} - \xi°_{m,s}$ is the difference of correlation functions between actual (ξ) and disordered ($\xi°$) states, the effective interaction parameters being defined by

$$\epsilon_{m,s} = \frac{1}{2^N} \sum_{J_0} \nu_{m,s}(J_0) \, E(J_0) \; . \tag{6}$$

The physical meaning of these interaction parameters can be illustrated for the case of pairs (m=2). We have, for the particular pair joining points p and p':

$$\varepsilon_{pp'} = \frac{1}{2^2} \sum_{\sigma_p = \pm 1} \sum_{\sigma_{p'} = \pm 1} \sigma_p \sigma_{p'} \frac{1}{2N'} \sum_{J'} E_{\sigma_p \sigma_{p'}}(J') = \frac{1}{4}(V_{++} - V_{+-} - V_{-+} + V_{--}) \quad (7)$$

with

$$V_{ij} = \frac{1}{2N'} \sum_{J'} E_{ij}(J'), \quad (8)$$

with $N' = N-2$. Because of translational symmetry, the effective interaction does not depend on the location of the pair, only on its type s, so we have:

$$E_{2,s} = -\frac{1}{2} V(s) \quad (9)$$

with

$$V = V_{AB} - \frac{V_{AA} + V_{BB}}{2} \quad (10)$$

in the familiar notation (see for example Ref. [1]), where, for instance, + occupation represents an A atom, and − a B atom. It is apparent from the definition (8) that the quantity V_{ij} represents the total energy of an ij pair embedded in an average, random medium. The difference V thus represents a net or **exchange interaction** which is typically a very small fraction of the V_{ij} energies themselves. Hence, Eq. (10) cannot be used to compute the effective ordering energies themselves, since the V (or ε) are expressed as very small differences of almost identical very large numbers. Various schemes which have been suggested for getting around this difficulty will be reviewed, below.

Note that nowhere have we tried to express the cohesive energy as a sum of pair energies: according to Eq. (4), the total energy is written as sum of E_0, the cohesive energy of a random solid solution, plus a much smaller term, the ordering energy:

$$E = \sum_r N_r \varepsilon_r \xi_r \quad (11)$$

where N_r is now (N/2) times the number of neighbors in coordination shell r about a lattice point, the summation being limited, in practice, to a few coordination shells only. It is then clear, from Eqs. (7) and (8), that the effective interactions ε (or V) must depend on the average medium through the set of configurations J_0, hence they must be concentration dependent. In Sect. 7, we shall examine how such interaction parameters might be obtained from electronic band structure calculations. For the next two sections, however, we shall regard the pair interaction parameters as given constants. All of the physics of phase diagram prediction in the present context is contained in the sets of ε (or V) parameters.

4. ORDERED GROUND STATES

Before introducing the temperature dependence of alloy phase stability, it is necessary to determine what ordered superstructures are to be

expected at absolute zero, in other words, the question "what ordered ground states will be found for a given set of V parameters and for various compositions" must be answered. The correct superstructures are those which will minimize the ordering energy (11). Since, by Eq. (11), or (12), E is linear form, one must solve a linear programming problem, as the ξ variables are subject to certain constraints. First, the values of the correlations must lie between +1 and -1, then, since cluster concentrations must be non-negative, we have, by Eq. (2), the additional constraints:

$$1 + \sum_{m,s} \nu_{n,r;m,s}(J) \; \xi_{m,s} \geq 0 \qquad (13)$$

for all configuraitons J of the largest clusters (n,r) used. It turns out [6] that inequalities (13) define a "configuration polytope" in multidimensional ξ-space, the ratios of which, in principle, have ξ-coordinates which uniquely define the correct ordered ground states. Unfortunately, inequalities (13) may yield vertices which produce "non-constructible" structures, so that a "tighter" set of inequalities must be derived, which is not always feasible to do.

Early methods and bibliography are reviewed in Ref. [1] and [6]. All methods are based on linear programming techniques, although the inequalities and techniques of minimization may differ. Inequalities are derived through "cluster" considerations, as in (13). Completely solved problems include the ground states of fcc and bcc lattices with first and second neighbor pair interactions [7-9]. The case of the fcc lattice with V_1, V_2, V_3 and V_4 interactions has been partially solved [7], and so has the case of the fcc lattice with V_1, V_2, tetrahedron and octahedron multiatom interactions [6]. Recently [10], a very elegant computer code was developed and applied to the bcc lattice with V_1, V_2, V_3, and V_5 pair interactions.

Many experimentally observed ordered fcc superstructures, such as the $L1_0$, $L1_2$, $L1_1$, DO_{22}, Pt_2Mo, etc...have been predicted by the ground state analysis limited to V_1 and V_2. Other structures, such as the $D1_a$, require, in addition, 4th neighbor pair interactions for stability, as shown by Kanamori [7]. The complete list of fcc ground states and the ranges of the ratio $\alpha = V_2/V_1$ over which the various structures are stable have been given in many publications, such as [1], [3] and [6]-[9], with perspective drawings of the unit cells of the less symmetric structures illustrated in Ref. [11].

5. FREE ENERGY

It was seen that, at absolute zero, the state of order of, say, a binary solid solution is given by a vector ξ at the origin of multidimensional ξ-space and end point on the surface of the configurational polytope: at vertices in case of stoichiometric superstructures, at edges and faces, away from stoichiometry. At higher temperatures, the configurational entropy contribution favors some disorder so that the vector ξ no longer touches the surface of the polytope, but lies somewhere inside it. To determine equilibrium configurations, i.e. equilibrium values of the multiplet correlations, it is necessary to minimize the ordering free energy

$$F = E - TS \qquad (14)$$

where E, in general, is given by Eq. (11).

It was first shown by Kikuchi [12] that the configurational entropy S could be expressed by an increasingly accurate hierarchy of cluster approximations, known as the Cluster Variation Method (CVM). As the name

implies, the CVM is a variational technique, meaning that the free energy is written as a functional of cluster concentrations x, which functional must then be minimized with respect to the unknown x. The CVM entropy is found to be given approximately by a sum of partial "cluster" entropies s_ℓ:

$$S = N \sum \gamma_\ell s_\ell \qquad (15)$$

where the collective index ℓ has been used for (m,s), the sum in Eq. (15) running over all clusters and sub-clusters retained in the state-of-order description. The coefficients γ are positive or negative integers which may be obtained by geometrical considerations [12] or by recursive formulas [13,14]. The partial entropies are given by:

$$s_\ell = - k_B \sum_J x_\ell(J) \ln x_\ell(J), \qquad (16)$$

k_B being Boltzmann's constant.

Since by Eq. (2), the cluster concentrations are linear functions of the multiplet correlations ξ, the free energy (14) can finally be written as a functional of the independent ξ variables

$$F = F(\xi_1 \ldots \xi_\ell \ldots \xi_L) \qquad (17)$$

or, more explicitly, in the pair-energy approximation, for the free energy per lattice point,

$$f = \frac{F}{N} = \sum_r \omega_r \epsilon_r \xi_r + k_B T \sum_\ell \gamma_\ell \sum_J x_\ell(J) \ln x_\ell(J) \qquad (18)$$

in which ω_r is half the r-shell coordination number. Equation (18) is written for the disordered state, in which all lattice points are equivalent. In ordered states, a distinction must be made between various sublattices, on each of which points are equivalent. Thus, for ordered phases, the free energy expression (18) must be amended, as explained elsewhere [15], though no new principles are introduced.

Equilibrium is determined by minimizing (17) with respect to the (independent) variables ξ. Usually, this is carried out by Newton-Raphson iteration [2,15]. Actually, one minimizes the "grand potential" [16]:

$$w = f - \mu \xi \qquad (19)$$

where, for any ordered phase, ξ is a sum of point correlation variables over the sublattices, and μ is an appropriate difference of chemical potentials. For given μ and temperature T, the minimization then returns equilibrium values of the ξ correlations and hence, by Eq. (2), all desired cluster concentrations, including the average concentrations x_A and x_B.

6. PHASE DIAGRAMS

When an analytic form of the free energy, as Eq. (18), is known, much of the thermodynamics properties of the system can be derived, such as configurational energy, entropy, specific heat, etc. The vibrational contribution to these quantities is not available from the present model; however, it is reasonable to assume that, although strictly thermal effects can be as large or larger than the configurational ones, their differences, from one phase to another, at given temperature, will be small - recall

that the various ordered phases considered here (intermetallics) are superlattices of a given parent lattice.

A critical test for a free energy model is to see how good a (temperature-composition) phase diagram can be derived from it, and much effort has been expended over the last few years in calculating phase diagrams from CVM free energies.

The first such calculation was that of Van Baal [17] who considered first-neighbor pair interactions (V_1) on an fcc lattice, the tetrahedron cluster (T) approximation of the CVM being used in the entropy expression. Next, tetrahedron interactions were included in the internal energy expression (11), and a very good likeness of the Cu-Au phase diagram was produced [18]. Calcluated and experimentaly determined diagrams are also reproduced in Ref. [1], and compared to that obtained by the older Bragg-Williams (BW) model.

Next, second neighbor pair interactions were introduced so that both tetrahedron and octahedron (TO) clusters had to be used in the CVM entropy. The ferromagnetic (clustering) transition temperature at zero field (50/50 composition) calculated by the TO-CVM was found to differ by only 2% from that obtained by the best available high-temperature expansion [2]. By contrast, the BW approximation gives a result which is off by 22%.

The TO-CVM has been used to calculate a number of phase diagrams featuring the fcc ordered ground states proven to be stable for various values of the ratio $\alpha = V_2/V_1$. Hence, α is the only physical parameter which enters the calculations. In all, seven diagrams were computed for values $\alpha = 0.0, 0.25, 0.35, 0.45, 0.55, -0.2, -1.0$. These **prototype ordering phase diagrams** have recently been collected in an overview article [11], details of the calculations being given in Refs. [15], [19] and [20]. Since no real alloy system is expected to be well modeled by ordering energies depending on constant V_1 and V_2 pair interactions, the accuracy of the TO-CVM prototype diagrams could only be tested against available Monte-Carlo (MC) simulations of ordering in the fcc Ising model with first and second neighbor interactions. In general, MC and CVM results agree closely, particularly at first-order transitions [11,20]. The CVM tends to overestimate second-order transition temperatures, particularly away from stoichiometry. It should be noted, however, that the Monte Carlo results for $\alpha = 0.0$ are still somewhat controversial [21,22].

Only one prototype phase diagram is shown here, that for $\alpha = 0.35$ (Fig. 1, see Ref. [19] for a detailed description). Ordered superstructures labeled A_5B, A_3B, A_2B and A_2B_2 are, respectively, monoclinic, tetragonal, orthorhombic and tetragonal superstructures of fcc [11]. The dashed line is the stability limit of the disordered phase (or ordering spinodal [1,23]), at which (in the present case) a $\langle 1^1/_2 0 \rangle$ ordering wave just becomes unstable [1, 3, 23, 24]. Second-order phase transitions occur where phase boundaries (full lines) and instabilities (dotted lines) coincide.

Recently, Sanchez and collaborators have extended the CVM calculations to include ordering energies obtained by Lennard-Jones potentials. This procedure effectively results in concentration-dependent ordering energy parameters; the lattice parameter also varies with concentration. This method has been successfully applied to mapping the experimentally determined Ni_3Al phase boundaries [25], and to producing "incoherent" prototype phase diagrams exhibiting fcc and bcc superstructures and miscibility gaps. The interesting problem of completing "ionic" and magnetic ordering has also been investigated [27]. A new formulation [14] of the CVM and various applications have also been reviewed recently by Sanchez and co-workers [28].

7. ELECTRONIC BAND STRUCTURE CALCULATIONS

From the foregoing, it is apparent that the statistical mechanical machinery is in place for calculating reliable configurational free energies, and hence realistic phase diagrams. To make the calculations truly predictive, it would be necessary to derive the V_1, V_2, ... interactions from first principles. It was seen that the "cluster" concept was essential for describing states of partial order, for determining ground states superstructures, and for calculating the configurational entropy. It is therefore expected that clusters may play an important role in fundamental electronic energy calculations as well.

7.1. Basic Formulation

It is a fairly straightforward matter to formulate the problem of calculating the cohesive energy of a metal or alloy: one writes down the total Hamiltonian in the form [29]:

$$H_t = K_e + K_n + V_{en} + V_{ee} + V_{nn} \qquad (20)$$

when K_e and K_n are the kinetic energies of the electrons (e) and nuclei (n), respectively, V_{en} is the electron-nuclei interaction, V_{ee} is the electron-electron interaction, and V_{nn} is the nuclei-nuclei interaction. The K_n term, which can be handled semi-classically, contributes to the vibrational entropy and will not concern us here. Likewise, the Coulomb nuclear repulsion term (practically, an ionic repulsion term) can be treated classically and added on after the quantum mechanical calculations have been performed. The terms K_e must be written in differential operator form and combined with V_{en} and V_{ee} to produce a strictly "electronic" Hamiltonian H, to be used in the Schroedinger equation:

$$H\Psi = E\Psi \qquad (21)$$

where Ψ is the wave function and E the associated energy eigenstate.

Without drastic simplifications, Eq. (21) cannot be solved, the V_{ee} electron-electron interaction representing a major difficulty. Several schemes are now available for reducing the problem to an equivalent one-electron problem, the most popular one being the local density functional method (see for example Ref. [29]). Even so, the absolute magnitude of certain important physical parameters are predicted incorrectly unless more elaborate corrections are carried out [30]. It is believed, however, that these corrections will not be required in the calculation of relative quantities such as ordering energies, which we are concerned with here.

Solving Eq. (21) in an effective one-electron approximation with periodic potential (for pure or fully ordered crystals) still presents a formidable problem. Various approximate methods are available, the most useful one for alloy calculations being the tight binding (TB) and Korringa-Kohn-Rostoker (KKR) methods. These and other techniques are described in Ref. [29], and also by Pettifor, in a particularly readable account [36]. Basically, the tight binding is used as an approximation valid for transition metals if it is assumed that nearly all of the binding energy is provided by electrons in the d band. The KKR is of more general applicability (s, p, d electrons) and is based on multiple scattering theory. If f electrons participate in the bonding (heavy nuclei), relativistic effects must be taken into account, so that the appropriate

differential equation to solve is no longer the Schroedinger, but the Dirac equation, thereby further complicating the problem.

Actually, for cohesive energy calculations, the wave function itself is not required; what is needed is the eigenvalue spectrum of the operator H, i.e., the density of states (DOS), the spectrum being virtually continuous. The total electronic energy is then obtained by filling up the DOS with electrons according to the Fermi-Dirac distribution. Techniques for carrying out this computational program are now under control. Impressive applications of such calculations to elemental solids or stoichiometric compounds are, for example, those of Moruzzi, Williams and Janak [31] or those of Cohen and collaborators [32] who use the pseudopotential method. Accurate absolute zero values have been obtained for the lattice parameter, elastic moduli and cohesive energy. Usually, the crystal structure is assumed, but in some cases [33], it has been possible to perform the calculations for various crystal structures to see which one gave the lowest energy; often, though not always, the correct structure was predicted. High accuracy is required, of course, as energy differences between competing structures are usually very small. In favorable cases, then, a true **first principles calculation** was performed: physical properties were derived from a knowledge of the atomic number Z alone.

7.2. Single-Site CPA

For pure crystals and stoichiometric compounds, all of the crystallographic information is contained in the unit cell, and translation symmetry reduces the computational problem to manageable proportions. In the case of alloys, the disordered nature of the system precludes the use of such simplifications. Since it is out of the question to perform the required quantum mechnical calculations on all possible configurations of a (large) representative region of the disordered crystal, it is imperative to attempt to restore translational symmetry by suitable averaging techniques.

As was mentioned in connection with the state of order description (Sect. 2), if complete disorder is assumed, it is sufficient to regard the lattice sites as being occupied by identical "average atoms". In this "point" approximation, the question is: how does one define an average atom? In the regular solution or Bragg-Williams free energy models, each lattice site is assumed to be occupied by an average atom of concentration x_B (or x_A), given by the average concentration on the given lattice or sublattice. In electron theory a lattice site must be occupied by an "average atom" having sensible physical properties, in other words, one must associate with each site an appropriate potential $V_{av}(r)$, function of postion r, which can properly scatter electrons. Following the BW idea, the simplest procedure consists in setting:

$$V_{av}(r) = x_A V_A(r) + x_B V_B(r), \qquad (22)$$

where V_A and V_B are the A and B atomic potential, respectively. Such is the so-called **virtual crystal approximation** which has been shown to yield unreliable results, particularly for transition metal alloys [29].

Electronic structure calculation on fully disordered systems improved considerably with the advent of the coherent potential approximation (CPA). For a review, see Ref. [34], for example. The density of states can be obtained directly from the Green's function, the operator that is inverse to the Hamiltonian of Eq. (21). Actually, an average Green's function $\langle G \rangle$ is required, i.e., averaged over all configurations. The function $\langle G \rangle$ is then written as the inverse of an effective Hamiltonian H_{eff} which is expressed

in terms of an effective potential $w(r)$, which is the same at every site. In such a way, an effective medium is created which possesses translational symmetry. The problem now consists in calculating the scattering of an electron off a real atomic potential, V_A or V_B, imbedded in the CPA medium. The effective potential w is chosen in such a way that the replacement of the average potential by a real one at a given site causes no change in the scattering. This requirement leads to the basic CPA equations which must be solved self-consistently.

7.3. Cluster CPA

The CPA has been found to give satisfactory results in those cases for which comparison could be made with exact calculations [29, 34]; it is thus regarded as the best available single-site approximation, valid for complete compositional disorder. As such, this approximation cannot begin to do justice to the complexities of order-disorder phenomena any more than the regular solution model of statistical thermodynamics is able to handle order-disorder reactions.

It is possible to treat long-range order through the so-called "inhomogeneous CPA" which is to the "point" (homogeneous) CPA what the Bragg-Williams model is to the regular solution: the trick is to subdivide the lattice of the disordered state into distinct sub-lattices, and perform "point" CPA's on each. The inhomogeneous CPA is thus still a single-site approximation; short-range order cannot be treated in this framework, nor is it possible to obtain values for the ordering interactions V_n.

As anticipated, the richness of order-disorder phenomena can only be produced from a theory which can handle states of partial order, i.e., from theories which are based on cluster methods. Ideally, one would like to do for electronic theory what the CVM has done for the statistical aspects of ionic ordering. Despite repeated efforts, a fully self-consistent Cluster-CVM remains, as of this writing, an elusive goal. A fundamental difficulty is that quantum mechanical operators must be dealt with rather than the simple scalars of the ordinary CVM. Nevertheless, some progress has been made, as will be now briefly described.

Gonis and Freeman [37] list three types of cluster-CPA models: (I) cluster theories in which the average medium reflects the cluster configurations in a self-consistent way, (II) cluster theories in which the cluster is embedded in a medium determined in a non self-consistent way, and (III) cluster theories in which the cluster is embedded in a medium that is determined in some self-consistent way which involves clusters smaller than the embedded one. If the medium cluster is a single-site, the average medium is then that of the single-site CPA.

The latter method has been used to calculate the DOS of a one-dimensional "alloy" exhibiting various degrees of short-range order (SRO), described by either positive (clustering) or negative (ordering) nearest neighbor pair correlations. Clusters of various sizes (one to nine points) were embedded in both single-site and pair-site CPA media. Calculations were performed for a single-band tight-binding Hamiltonian and compared to exact results obtained by direct summation of energy eigenvalues for systems of various configurations having chosen SRO values. It was shown [37] that, particularly with the larger clusters, the embedded cluster method reproduced the considerable complexities of the exact DOS to a remarkable extent.

Gonis, Stocks, Butler and Winter [38] used method III in an fcc binary alloy choosing, as embedded cluster, a central site and its 12 nearest neighbors (cuboctahedron), the effective medium being that of the

self-consistent single-site CPA. A muffin-tin Hamiltonian was used and the calculations were performed in the KKR framework, the complications of electron-electron interactions having been neglected. The authors believe, as was surmised above, the V_{ee} corrections to be relatively unimportant when ordering energies are required. To express the average internal energy given above by Eq. (2) in terms of the embedded cluster formalism, let us focus on a particular (central) fcc lattice point (p_0) of the crystal and its coordination shell of first nearest neighbors. The expectation value of the energy can then be written as:

$$\langle E \rangle = \sum_J X(J)E(J) = \sum_j x(j) \sum_{J'} X(j,J') \, E(j,J') \tag{23}$$

where $x(j)$ is the probability of finding, in the ensemble of systems, a 13-point cluster centered at p_0 having configuration j, $X(j,J')$ being the probability of observing configuration J' outside the central cluster, given that the latter has configuration j. If it is assumed that correlations do not extend much beyond the first coordination shell, we may take this conditonal probability to be approximately independent of j, so that we may write:

$$\langle E \rangle = N \sum \, [x_{A,z}E_{A,z} + x_{B,z}E_{B,z}] \tag{24}$$

where

$$E_{i,z} = \frac{1}{N} \sum_{J'} X(J') \, E(i,z;J') \tag{25}$$

and where the index j has been replaced by the double index i (= A or B, for the central atom) and z (denoting the first-shell configuration). In Eq. (24), $x_{i,z}$ has the same meaning as $x(j)$ in Eq. (23).

The energy defined by Eq. (25) is the energy per site of a crystal having atom i at the point considered when surrounded by a particular first-shell configuration z. That energy can be calculated from the corresponding local DOS $n_{i,z}$ as follows [39].

$$E_{i,z} = \int_{-\infty}^{E_F} E \, n_{i,z}(E) \, dE \tag{26}$$

where E_F is the Fermi energy determined by the CPA. In the single-site approximation, Eq. (24) would give simply:

$$\langle E \rangle = x_A E_A + x_B E_B = E_0, \tag{27}$$

where E_0 is the random-solution energy defined by Eq. (5). Note that, despite a superficial resemblence, Eqs. (27) and (22) mean very different things. An expression similar to the one in square brackets in Eq. (24) has been used by Gonis, Butler and Stocks [39] to evaluate approximate ordering energies in a 50/50 AgPd alloy. To obtain correct energies, in partially disordered states, one would have to know, at given temperature and average concentrations, all probabilities $x_{i,z}$, of which there are 288 distinct ones [40], and calculate all corresponding energies $E_{i,z}$. This is a formidable undertaking which, not surprisingly, has not been carried out.

Gonis et al. [38, 39] did obtain, however, some extremely interesting and promising results for the local DOS $n_{i,z}$ for selected first-shell configurations z in AgPd. The various computed $n_{i,z}$ clearly exhibited the expected results for partially ordered systems. In particular, the pure-Ag or pure Pd cluster DOS resembled those of the pure elements, while that of, say, Pd surrounded by an all-Ag shell exhibited a single peak characteristic of a single impurity embedded in a pure medium, though somewhat broadened by the disorder [38].

7.4. Generalized Perturbation Method

These are encouraging results; unfortunately it is not clear how to extract directly from the cluster CPA the various V_n effective interation parameters required by statistical thermodynamic theories, such as the CVM. Hence, the generalized perturbation method (GPM) of Gautier and Ducastelle [42-47] may turn out to be more convenient. In this approach, the energy of a given alloy configuration is expressed by a "cluster expansion" of the reference medium E.

$$
\begin{aligned}
E(\{\gamma\}) = E_0 &+ \frac{1}{2} \sum_{i \neq j} V(p_i p_j)\gamma(p_i)\gamma(p_j) \\
&+ \frac{1}{3} \sum_{\substack{i \neq j \\ j \neq k \\ k \neq i}} V(p_i p_j p_k)\gamma(p_i)\gamma(p_j)\gamma(p_k) \\
&+ \frac{1}{4} \sum_{\substack{i \neq j, j \neq k \\ k \neq \ell, \ell \neq i}} V(p_i p_j p_k p_\ell)\gamma(p_i)\gamma(p_j)\gamma(p_k)\gamma(p_\ell) + \ldots
\end{aligned}
\tag{28}
$$

In this expansion, the occupation variables are defined [1] as the deviation from the average concentration ($c = x_B$) of the occupation (1 or 0) of site p_i, and the V are effective cluster interactions. By taking an ensemble average of (28), one recovers an expression similar to Eq. (4), with the ensemble averaged γ's related linearly to the correlations ξ [Eq. (1)] and pair interactions $V_{ij} = \langle V(p_i p_j)\rangle$ having the same meaning as the quantities defined by Eqs. (7) - (10). The multisite interactions differ somewhat from the effective cluster interactions of Eqs. (4) and (6): the restrictions on the summations in Eq. (28) indicate that the multisite interactions involve paths along clusters of points, over which steps may be retraced. The ensemble average of E_0 is just E_0 itself, the energy of the reference medium, calculated as that of the single-site CPA medium; it is identifed with the corresponding term in Eq. (4), the energy of the completely disordered state. Both in Eqs. (4) and (28), the reference energy E_0 is seen to depend on concentration, as do the interactions V themselves arising, as they do, from the expansion of the reference state. It is indeed because the energy of the reference medium is in some sense "close" to that of the actual configuration considered that expansion (28) converges rapidly. Calculations based on a tight-binding Hamiltonian have shown [46] that pair interactions are dominant. In particular, for fcc transition metal substitutional alloys, it was found that, in general, $|V_1| \gg (|V_2|, |V_3|, |V_4|) \gg (|V_5|, |V_6|)$ (the index indicating first, second...neighbor separation) [46], [48], but with V_4 (in magnitude) of the order of V_2 but larger than V_3. For bcc, one has, in general, $|V_1| > |V_2| \gg |V_3| = |V_5| > |V_4|$. Ducastelle and co-workers [48, 49, 50]

have also shown by performing moment expansions of the density of states, that the V_n pair interactions must necessarily change sign a number of times as a function of d-band filling. This implies that, for certain ranges of concentration in certain transition metal alloys, e.g., V_1 must become very small so that V_2, say, will become the dominant interaction.

Studies by the French school have also shown that multisite interactions are generally negligible in magnitude compared to pair interactions. In certain cases, however, cluster interactions involving self-retraced path may become important. Most importantly, calculations have shown that, although V_1 is generally expected to be larger than V_2 for substitutional alloys, the reverse can be true for off-stoichiometric interstitial compounds [48, 49]. This explains why such structures as "A₅B" [Fig. 1] or "CuPt" (see, for example, Ref. [11]), which require V_1, in magnitude, comparable to V_2, are far more common in interstitial sublattices than in substitutional fcc lattices.

In the TB approximation, it is in fact possible to express the pair interactions in transition metal alloys analytically as [44]

$$V_n = W \, V_n(c, \, N_d, \, \delta_d, \, \delta_{nd}) \qquad (29)$$

where c is the average concentration, N_d is the number of electrons in the d band, and where δ_d and δ_{nd} are the so-called diagonal and off-diagonal disorder. The average d band width W appears in Eq. (29) merely as a scale factor. In this approximation, Eq. (29) thus enables one to predict transition metal alloy ground state superstructures, since these are known as a function of $V_1 ... V_*$ from the work of Kanamori and co-workers [9]. In this way, Gautier and collaborators [44, 47] have produced a remarkable structural map showing predicted regions of stability of various common fcc superstructures as a function of the parameters N_d and δ_d, for various concentrations c. These extremely important results are also summarized by Pettifor [36]. Agreement with experimental data is, in most cases, satisfactory.

The possiblity offered by Eq. (29) of computing the V_n pair interactions directly from band structures is an exciting one, leading to ordered ground states and even phase diagram predictions. It would be desirable, however, to check the pair interaction values experimentally, or better yet, the densities of states themselves. Ways of doing this are described briefly below.

8. EXPERIMENTAL VERIFICATION

Ideally, one would like to obtain direct experimental evidence of densities of state. This is a very difficult undertaking, especially in the case of alloys; but two techniques are becoming available for carrying out such a program: angle-resolved photoemission and positron annihilation spectroscopy.

An application of the former method has been used by Jordan et al. [51] to ordered and disordered Cu₃Au. DOS spectra were obtained at various temperatures and compared to those calculated ab initio by fully relativistic (ordered state) and semi-relativistic (disordered state) KKR CPA formalisms. The disappearence, at higher temperatures, of small ordered state peaks were correlated in both theoretical and experimental DOS [51]. The technique is thus promising, but suffers from the serious drawback that only electron states near the surface of the specimen are sampled which, because of alloy surface segregation problems, may not be representative of the bulk.

Positron annihilation spectroscopy does not have the latter disadvantage and appears to be quite well suited for the study of the Fermi surface of metals and, particularly, of alloys (for reviews, see Refs. [52] and [53]). However, studies of electronic structure in general will require careful differentiation of effects due to point defects, particularly vacancies.

Values of the effective interaction parameters V_n themselves may be determined by comparing experimental and theoretical values of short-range order intensity (ISRO) fluctuations in disordered solid solutions, particularly just above a transition temperature. The art of measuring ISRO entails measurements of (x-ray or Neutron) diffuse diffracted intensity in substantial regions of reciprocal space, followed by fairly complex corrections for displacement effects. For a review of the current methods, see Ref. [54], for example.

Theoretical expressions for ISRO can be obtained by applying the fluctuation-dissipation theorem to whatever analytical free energy model one wishes to consider. At any point k in the first Brillouin zone, $I_{SRO}(k)$ is proportional to the expectation value of the Fourier transform X_1 of the point correlation function ξ_1 [55]:

$$I_{SRO}(k) \sim \langle |X_1(k)|^2 \rangle = \frac{k_B T}{N} (F^{-1})_{11} \qquad (30)$$

where $(F^{-1})_{11}$ is the first element of the inverse of the Fourier transform of the matrix of second derivatives of the free energy with respect to correlation variables. Equation (30) is exact, and would yield exact results if an exact free energy were available. For the one-dimensional Ising model with nearest neighbor interactions, the condition of conservation of integrated intensity is rigorously obeyed [55] if the CVM free energy is used. For higher dimensional systems, the CVM integrated intensity no longer has the required property, but does significantly better than that derived by BW models, such as the Krivoglaz and Clapp-Moss formulas (for a review of BW derivations, see for example Ref. [1], and references cited therein).

Recently, CVM and BW calculated ISRO were compared for the fcc Ising model with first (V_1) and second (V_2) neighbor (constant) pair interactions. Contours of constant intensity in a (001) section of reciprocal space are shown in Fig. 2, calculated according to the Sanchez formula (CVM, left frame) and the Krivoglaz-Clapp-Moss (KCM) forumla (BW, right frame), for the case of $\alpha = V_2/V_1 = 0.35$, at temperature $T = T_0/0.95$, where T_0 is the instability temperature, indicated by the dashed line at the chosen concentration of $c = 0.5$ in the phase diagram of Fig. 1. It is seen that the CVM diffuse intensity peaks at $<1\ ^1/_2\ 0>$ are much sharper than those of the BW calculation. The differences may not appear that dramatic, but the sharpness of the CVM peaks insure a more nearly constant integrated intensity at all temperatures except very close to the instability T_0. Furthermore, the ISRO calculations (Fig. 2) are completely consistent with the calculated phase diagram (Fig. 1) which, at least for $\alpha = 0.25$, is known to agree closely with that obtained by Monte Carlo simulations (see Ref. [11]).

Up to now, the KCM has been used exclusively for extracting pair interactions from diffuse intensity measurements: the procedure consists in choosing the correct set of V_n in an attempt to reproduce theoretically the experimentally determined intensity contours (see Ref. [56], for example). A simpler method would be to use the author's fcc and bcc "eigenvalue tables" [23] to fit major and minor axes of closed intensity contours about

diffuse intensity peaks. The resulting V_n values are only as good as the BW model itself, however, which is not good at all for fcc-based ordering systems.

A very interesting comparison of back-calculated V_n values obtained by CVM and BW methods has just been performed. The technique used has been called the "inverse CVM" [57], and was first suggested to the author by E. Van Royen [58]. It is, in a sense, an extension of Clapp's Probability Variation method (PVM) [40], itself an offshoot of Kikuchi's CVM (see, for example pg. 247 of Ref. [1]). As in the PVM, one must assume that the internal (ordering) energy can be expressed by means of pair interactions alone, as in Eq. (12), the V's and ε's being related simply by Eq. (9). At equilibrium, the corresponding CVM free energy, Eq. (18) must be minimized, with pair correlations ξ_r being known from experiment, but with unknown interaction parameters ϵ_r. Equation (18) can be written equivalently, by means of Eq. (2), as

$$f = \sum_r \omega_r \epsilon_r \xi_r - T\, s(\xi_1 \ldots \xi_n, \zeta_1 \ldots \zeta_L) \qquad (31)$$

where s designates the configurational entropy per lattice site, expressed as a function of the n (known) pair correlations ξ_n and L (unknown) multiplet correlations ξ_ℓ. The equilibrium conditions are [2]

$$\frac{\partial f}{\partial \xi_r} = \omega_r \epsilon_r - T\, \frac{\partial s}{\partial \xi_r} = 0 \qquad (32a)$$

$$\frac{\partial f}{\partial \zeta_\ell} = - T\, \frac{\partial s}{\partial \zeta_\ell} = 0 \qquad , \qquad (32b)$$

since the correlation variables are independent. Equations (32b) represent a maximum entropy condition, just as in the PVM, which return the equilibrium multiplet correlations. These values are then inserted into (32a) along with given ξ_r, yielding s*, say, from which the required interactions (ε or V) can be obtained directly:

$$\epsilon_r = \frac{T}{\omega_r} \frac{\partial s^*}{\partial \xi_r} \quad (r = 1, \ldots n) \qquad (33)$$

In a recent study [57], [59], pair correlations in an fcc lattice were determined "experimentally" by Monte Carlo simulation with up to fourth-neighbor pair correlations. The set $V_1 \ldots V_4$ was then back-calculated by the inverse CVM in the "quadruple tetrahedron" approximation. The CVM interactions were found to agree much more closely with the MC input values than did those calculated by the BW model.

In another recent development, Gyorffy and Stocks [60] have performed first-principles KKR-CPA calculations of ISRO in one-dimensional disordered systems and have also confirmed the existence of flat portions in the (3-Dim) Fermi surface of CuPd alloys for certain ranges of average concentrations. This latter calculation predicts, in the disordered state, the wavelength on long-period modulations as a function of concentration in excellent agreement with experimental observations.

It is clear that diffraction methods, coupled with CVM ISRO analysis in partially ordered crystals can, in principle, yield reliable values of V_n interactions, which may then be compared to theoretical values obtained, for instance, by the Generalized Perturbation Method of Gautier, Ducastelle and co-workers. It is also expected that synchrotron radiation will play an

increasingly important role (a) by providing high-intensity, high-resolution ISRO data and (b) through angle-resolved photoemission spectroscopy, by providing insight into the electronic density of states itself.

9. DISCUSSION: TOWARDS A GENERAL ALLOY THEORY

It should be clear from the foregoing that, if the unit cell is the fundamental structural unit for elemental crystals and stoichiometric compounds, and the lattice point that for completely disordered solid solutions, the cluster of points is the fundamental unit for partially ordered crystals. Cluster methods are indispensable to characterize the state of order (Sect. 2), to predict ground states of order (Sect. 4), to approximate the configurational entropy (Sect. 5). In combination, these cluster methods culminate in the calculation of "prototype" ordering phase diagrams (Sect. 6) constructed with given, fixed sets of pair interactions, V_n.

The internal energy also can be expressed in terms of cluster expansions (Sect. 3). If one could calculate reliably cluster interactions, pairs primarily, from electronic band structure theories, one would obtain, from first principles, the free energy, configurational entropy, specific heat, SRO, LRO, diffuse intensity (Sect. 8), phase diagrams, etc.. for those alloy systems which can be described fairly well by Ising models. Presently, the most critical problem of course remains that of calculating the DOS of alloys with sufficient accuracy.

It is not surprising that cluster methods play an important role in electronic energy computations. In fact, a parallel can be established between statistical models and band structure methods (Sect. 7):

Level 1: Regular Solution Model   ←→ Single-Site CPA
Level 2: Bragg-Williams Model   ←→ Inhomogeneous CPA
Level 3: Cluster Variation Method   ←→ Cluster CPA, or Generalized
                                                   Perturbation Method.

A complete **Alloy Theory** must operate at Level 3; it should integrate the CVM and the CPA, ideally in a self consistent loop, as was done initially by Kittler and Falicov [61,62] on simple models. The CVM is well under control, although, in practice, calculations are limited to small clusters, and numerical convergence of the algorithms often poses serious problems. On the electronic theory side, the CPA appears to be very promising as a means of calculating the all-important V_n effective pair interactions which constitute the major input for ground state calculations and the CVM free energy. For phase diagram computations, the average energy E_O must also be known as a function of concentration and perhaps atomic volume. Thus far, the GPM has been formulated in the tight-binding approximation, limiting its application strictly to transition metal alloys for which only d-electron states need be considered. Furthermore, the alloy elements must be non-magnetic, unless one wished to perform CVM calculations involving both magnetic and ionic ordering. Finally, T-B calculations are model ones, hence not truly of the "first-principles" category.

By contrast, the KKR-CPA used in conjunction with a muffin-tin Hamiltonian can be regarded as a truly first-principles method, not limited to transition metal alloys. Codes have even been developed for the heavier elements which require a relativistic approach [63]. Unfortunately, even in the single-site CPA version, calculations are very laborious and require considerable supercomputer time. Cluster CPA codes are even more elaborate

and, despite recent successes, do not yield directly the effective V_n interactions. What would be required is the implementation of the generalized perturbation method in the KKR-CPA framework, which is not a trivial undertaking [64].

Still, if, as a first approximation, the effect of atomic displacements can be neglected (dynamic and static), the exciting possibility exists today of predicting thermodynamic properties and phase diagrams, for certain classes of binary alloys (AB), strictly from first principles, i.e., from a knowledge of the atomic numbers Z_A and Z_B only. Best candidate systems include those phase equilibria involving only superstructures of a given parent lattice. This limitation may not be as restrictive as it may appear: even in alloy systems featuring stable "incoherent" intermetallic compounds, the first product of solid state precipitation reactions generally consist of "coherent" superstructure phases, for which little experimental information is available, but which often determine final and are thus of crucial importance for the alloy designer.

In conclusion, a General Alloy Theory is an idea whose time has come.

ACKNOWLEDGEMENTS

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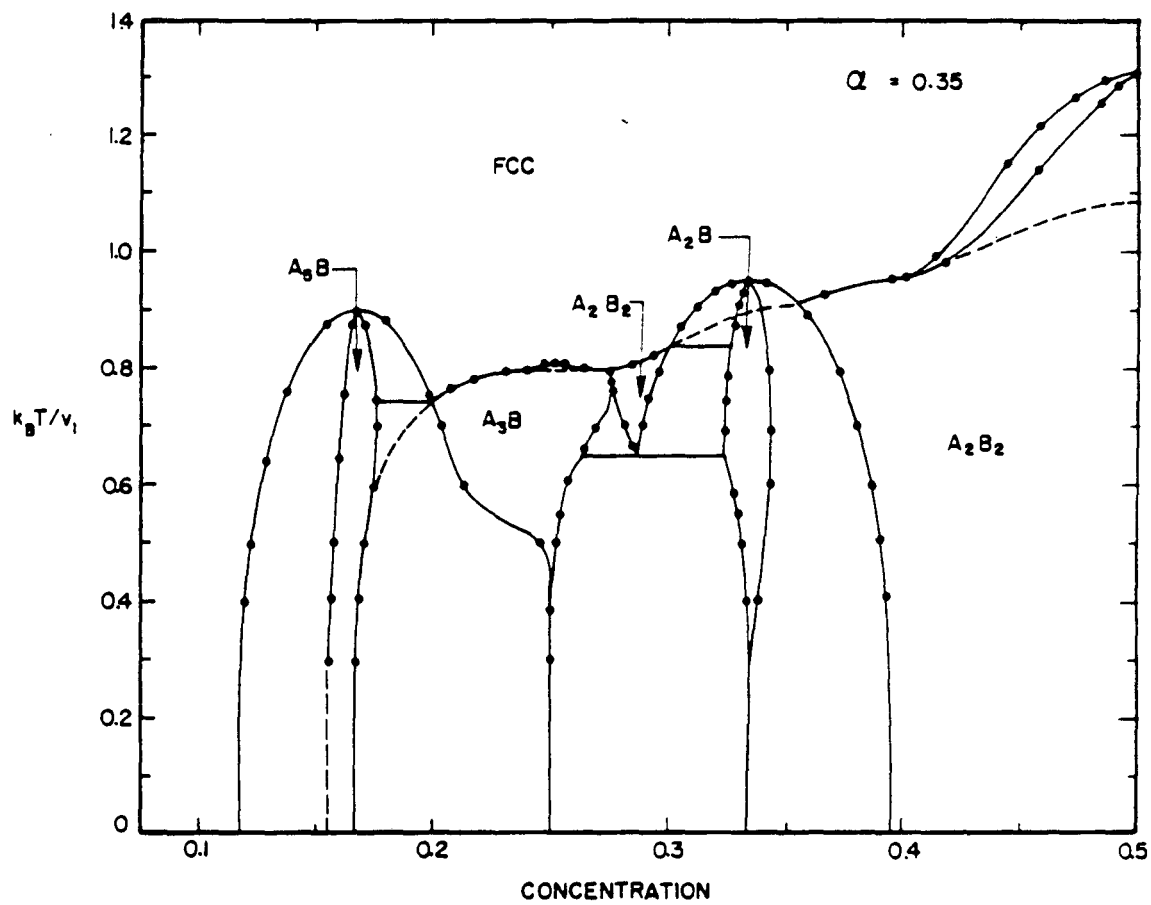
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FIGURE CAPTIONS

Fig. 1   Prototype ordering phase diagram calculated by the TO aproximation of the CVM with $\alpha = V_2/V_1 = 0.35$ [15]. Dashed line is $\langle 1\ ^1/_2\ 0 \rangle$ instability.

Fig. 2   Equal SRO intensity contours in a (001) reciprocal lattice section calculated for $\alpha = 0.35$, at $c = 0.5$ and $T = T_0/0.95$, where T_0 is the instability temperature (see Fig. 1). The left frame is based on the CVM and the right on the BW approximations.
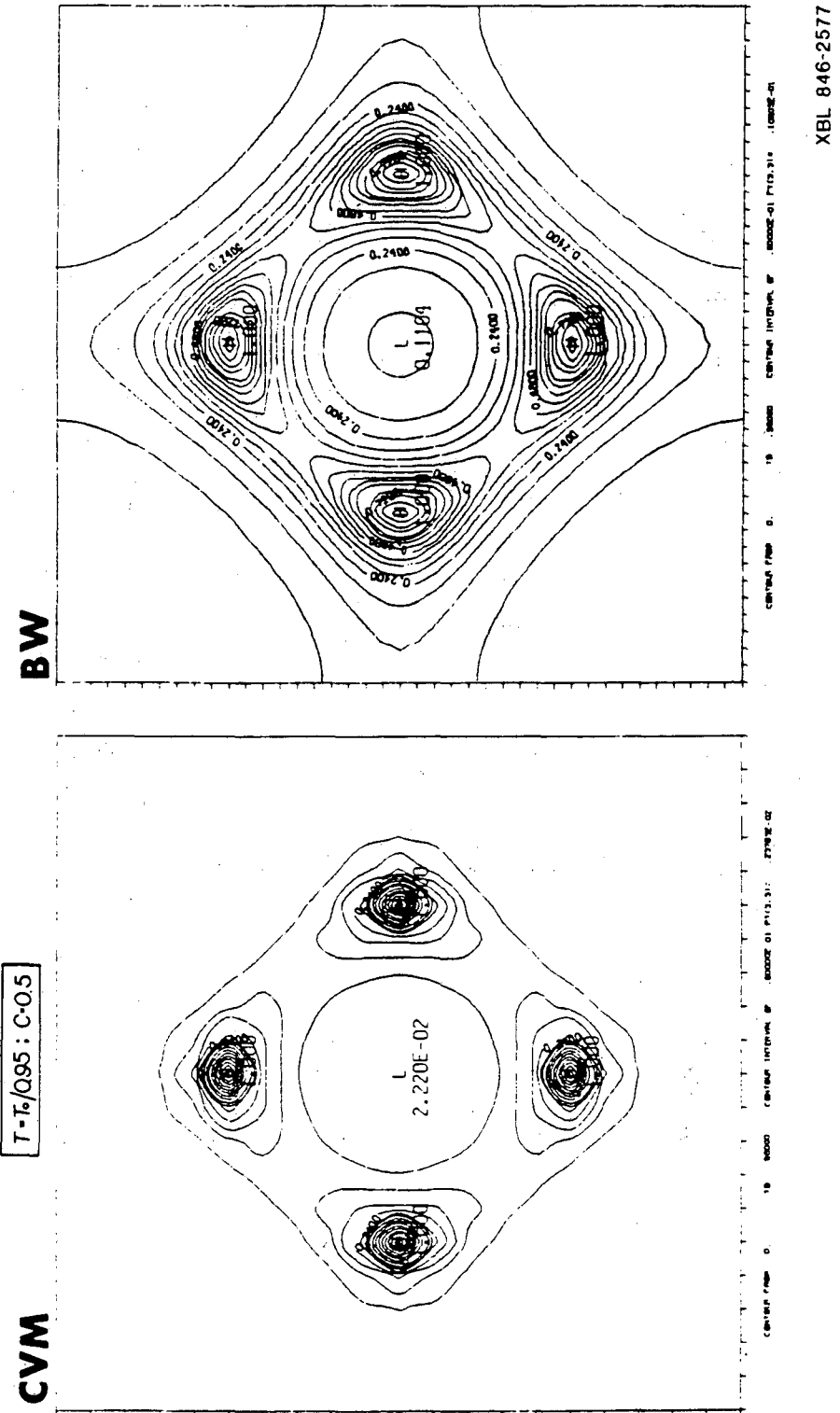
Fig. 1

CVM

$T - T_c/Q95 : C-0.5$

L
2.220E-02

BW

0.2400

0.2400

L
0.1184

XBL 846-2577

Fig. 2