RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 37, NUMBER 10 1 APRIL 1988

First-principles study of ordering properties of substitutional alloys using the generalized perturbation method

P. E. A. Turchi, G. M. Stocks,* W. H. Butler,* D. M. Nicholson,* and A. Gonis
Lawrence Livermore National Laboratory (L-280), P.O. Box 808, Livermore, California 94550

(Received 15 June 1987; revised manuscript received 1 December 1987)

Ab initio calculations of effective cluster interactions which make up the ordering energy of a substitutional alloy are reported. Tendencies toward ordering or phase separation and more generally phase stability in PdV and PdRh substitutional alloys are discussed. The study is based on an extension of the generalized perturbation method to systems describable by muffin-tin Hamiltonians in the framework of the multiple-scattering formalism in conjunction with the Korringa-Kohn-Rostoker coherent potential approximation. Future applications of the method are discussed.

The basic tools for studying ordering and phase stability in alloys, chemical short-range and long-range order, and ultimately alloy phase diagrams are essentially based on the so-called generalized three-dimensional (3D) Ising model, within various approximations, at $T \neq 0$ K. Among others, we can mention the cluster variation method (CVM)[1] and Monte Carlo simulations.[2] It is assumed in these models that the internal energy can be written as a rapidly convergent sum of pair and multisite interactions. This statement is clearly justified for normal metals and their alloys[3] using pseudopotential theory, but it has not been proved up to now whether or not such an expansion is still applicable for the total energy[4] in the case of possible strong disorder effects such as can be present in transition-metal alloys.

Because the validity and the success of phenomenological theories for the study of ordering processes have been noticed for a long time, extensive efforts have been made to provide a proper connection between electronic band-structure calculations and statistical models. Among other approaches, one can mention the concentration functional theory of ordering developed by Gyorffy and Stocks[5] and the embedded cluster method (ECM) of Gonis *et al.*[6] An alternative way to solve the problem is to derive a perturbation treatment starting from a reference medium which is close enough to any particular configuration of the alloy. Hence, the natural idea is to use the completely disordered state, as the one described within the coherent potential approximation (CPA), as an appropriate reference medium. Such is the essence of the generalized perturbation method (GPM) first introduced by Ducastelle and Gautier.[7] Further studies in the framework of the tight-binding approximation (TBA) along this line clearly proved, at least as far as general tendencies were concerned, that the TBA-CPA-GPM is a pertinent approach to study phase stability at $T = 0$ K for coherent and noncoherent ordered phases.[8] Furthermore, the preliminary calculations of phase diagrams based on the use of the TBA-CPA-GPM effective interactions to describe the ordering energy on one hand and the CVM to calculate the configurational equilibrium free energy on the other showed that the main features of coherent and noncoherent phase diagrams could be obtained.[9] Because of the different orders of magnitude involved in the calculation of the terms which make up the total free energy, it is of crucial importance to improve the determination of the internal energy, i.e., to define a more suitable reference medium for the totally disordered state. This required accuracy needs quite elaborate band-structure calculations. It is now generally acknowledged that the Korringa-Kohn-Rostoker (KKR) CPA (Ref. 10) provides a reliable first-principles description of band structure and related electronic properties of disordered substitutional alloys and avoids the parametrizations used in the TBA-CPA. Moreover, the multiple-scattering formalism on which the KKR CPA is based, is general enough to allow the study of a wide variety of alloys, particularly of normal-metal–transition-metal alloys.

In the present paper, we report briefly the first derivation of the KKR-CPA-GPM and its application to the study of the tendencies toward ordering or phase separation in PdV and PdRh substitutional alloys. Because the KKR CPA has been reviewed extensively in the literature,[11] here we present a condensed derivation of the self-consistency condition of the method in a form which allows the introduction of the quantities needed in the GPM expansion of the ordering energy.

The CPA self-consistency equation can be formally written as[12,13] (for cubic systems and $L \leq 2$)

$$\sum_{i=A,B} c_i X^i_{n,L}, \delta_{nm} \delta_{LL'} = 0,$$

$$X^i_{n,L} = \Delta m_{i;n,L} (1 - \Delta m_{i;n,L} \tau^{c,nn}_{LL})^{-1} ,$$

where τ^c denotes the scattering path operator (Ref. 11), $\Delta m_{i;n,L} = m_{c;n,L} - m_{i;n,L}$ and m is the inverse of the "on the energy shell" scattering t matrix. As a guideline we note the formal analogy which exists between the KKR multiple-scattering formalism and the more widely used tight-binding method.[13]

The thermodynamic potential for an electron system is given by

$$\Omega(T,\mu) = U - TS - \mu N$$

where T, S, μ, and N refer to the temperature, electronic entropy, chemical potential, and number of particles, respectively. The configurationally averaged ground-state energy in the KKR CPA formulation within the local density approximation is written as[14]

$$\Omega(\mu)=\sum_{n\neq m}\frac{Z^2}{|R_n-R_m|}-\int_{-\infty}^{+\infty}d\epsilon\,\Theta(\epsilon-\mu)N(\mu)+\int_{-\infty}^{\mu}d\mu'\int_{-\infty}^{+\infty}d\epsilon\,\Theta(\mu'-\epsilon)\frac{\partial N(\epsilon,\mu')}{\partial\mu'}\ ,$$

where $N(\epsilon,\mu)$ stands for the configurationally averaged integrated density of states:[15]

$$N(\epsilon,\mu)=N_0(\epsilon)-\frac{Im}{\pi N}\mathrm{Tr}\ln\underline{\tau}^c+\frac{Im}{\pi N}\sum_i c_i\mathrm{Tr}\ln(1-\Delta m_i\underline{\tau}^c)\ .$$

Here the underlines refer to matrices in both site, n, and angular momentum $L=(l,m)$ indices and $N_0(\epsilon)$ is the integrated density of states for free electrons.

For simplicity, we consider the band-structure contribution to Ω:

$$\Omega_e(\mu)=-\int_{-\infty}^{+\infty}d\epsilon\,\Theta(\epsilon-\mu)N(\epsilon,\mu)\ .$$

For a particular configuration of a substitutional binary alloy, fully specified by the set $\{p_n^i\}$ of occupation numbers p_n^i ($p_n^i=1$ if site n is occupied by an i species, 0 otherwise), the band energy $\Omega_e(\{p_n^i\},\mu)$ can be written, by considering the expression of the integrated density of states, as a sum of two terms: (i) the concentration-dependent energy $\overline{\Omega}_e(\{c_i\},\mu)$ of the CPA reference medium (which is configuration independent) and (ii) a configuration-dependent energy $\Omega_e'(\{p_n^i\},\mu)$:

$$\Omega_e'(\{p_n^i\},\mu)=-\frac{Im}{\pi N}\int_{-\infty}^{+\infty}d\epsilon\,\Theta(\epsilon-\mu)\mathrm{Tr}\ln(1-\underline{X}\underline{\tau}^c)\ ,$$

where the trace is taken over the site and angular-momentum space.

In terms of operators, it has to be noticed that X is a site diagonal operator, whereas τ^c is a strictly nondiagonal operator in site indices. Expanding the logarithm, making use of the CPA condition for the case of binary alloys, $A_{1-c}B_c$, and of the definition $\Delta X=X^B-X^A$, we obtain

$$\Omega_e'(\{p_{n_l}^B\},\mu)=\sum_{k=2}^{\infty}\frac{1}{k}V_{n_1,\dots,n_k}^{(k)}\delta c_{n_1}\dots\delta c_{n_k}\ ,\quad \delta c_{n_l}=p_{n_l}^B-c\ ,$$

where the kth-order effective cluster interaction involving sites $n_1, n_2, \dots, n_k$ is given by

$$V_{n_1n_2\cdots n_k}^{(k)}=-\frac{Im}{\pi N}\int_{-\infty}^{+\infty}d\epsilon\,\Theta(\epsilon-\mu)\mathrm{Tr}(\Delta X_{n_1}\tau^{c,n_1n_2}\Delta X_{n_2}\cdots\Delta X_{n_k}\tau^{c,n_kn_1})\ .$$

Thus, to the lowest order in the perturbation, as far as the small parameter $|\Delta X\tau^c|$ of the theory is less than unity up to the Fermi energy, the quantity Ω_e' which is commonly called the ordering energy is given by

$$\Omega_e'=\tfrac{1}{2}\sum_s V_{os}^{(2)}\delta c_o\delta c_s\ ,$$

where V_{os} is the effective pair interaction between sites o and s:

$$V_{os}=V_{os}^{AA}+V_{os}^{BB}-2\,V_{os}^{AB}\ .$$

Therefore, at the Fermi energy, as far as the second-order terms of the expansion are the predominant ones, the positive (negative) sign of V_{os} clearly indicates a tendency toward ordering (phase separation). As in the case of tight-binding results,[8] these interactions are expected to depend on concentration, distance, and the input numbers of particles for both species.

To illustrate the method, we considered the cases of PdV and PdRh substitutional alloys based on an underlying fcc crystalline structure. For both systems, the calculations were performed on the basis of charge self-consistent CPA potentials, up to an angular momentum index l equal to 2. The fast contour integration method[16] has been used to calculate the effective cluster interactions at the Fermi energy of each alloy, at each concentration.

For both systems it has been found that the expansion of the ordering energy is rapidly convergent with most terms involving $k>2$, or distances larger than fourth neighbors for $k=2$, making almost negligible contributions to Ω_e'. This is mainly a direct consequence of the strong d character of the valence electrons and their directionality as well as disorder effects in these systems. Figure 1 shows the second-order contribution $V_n^{(2)}$, to the effective pair interactions for nth neighbors up to the fourth shell as a function of concentration for PdV alloys. By considering the appropriate combinations of effective interactions via the product $\delta c_o\delta c_s$ which specifies a given configuration (or state of order), and the possible ordered structures resulting from the search of the ground states

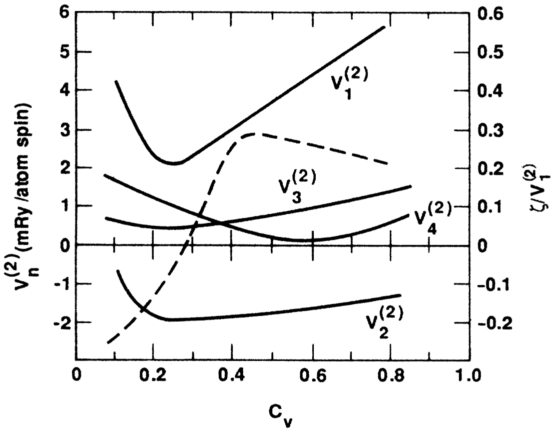

FIG. 1. Second-order term of the effective pair interactions up to fourth-neighbor shell (solid curves) and renormalized antiphase boundary energy, $\zeta/V_1^{(2)}=(-V_2^{(2)}+4V_3^{(2)}-4V_4^{(2)})/4V_1^{(2)}$, (dashed curve) as functions of vanadium atomic concentration for PdV substitutional alloy.

TABLE I. Ordering energies (expressed in mRy/atom spin) for various ordered structures of PdV.

Atomic composition	Type of order	Kanamori's notations (Ref. 17)	Ω_e'
Pd_8V	Ni_8Nb	· · ·	−0.580
Pd_4V	Ni_4Mo	15	−0.866
Pd_3V	Cu_3Au LI_2	17	−1.047
	Al_3Ti $D0_{22}$	18	−1.153
Pd_5V_2	Au_5Mn_2	19	−1.097
Pd_2V	$MoPt_2$	24	−0.728
PdV	CuAu I LI_0	39	−3.699
	CuPt LI_1	44	+1.607
	A_2B_2	40	−1.590
PdV_2	$MoPt_2$	24	−0.944
PdV_3	Cu_3Au LI_2	17	−3.336
	Al_3Ti $D0_{22}$	18	−2.104

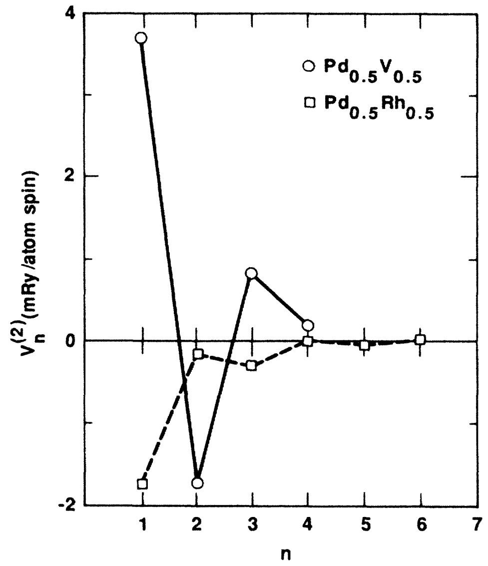

FIG. 2. Second-order term of the effective pair interactions as a function of distance, at $c=0.5$, for PdV and PdRh alloys.

of the Ising model,[17] it is possible to predict the most probable stable ordered structure at each concentration. Table I summarizes our results, valid at $T=0$ K, for the PdV system. Although the double counting and the Madelung energies, and the charge-transfer effects must give configuration-dependent contributions to Ω_e', our preliminary predictions are found to be qualitatively correct.

Taking account of pair interactions up to and including fourth neighbors, we predict a stable ground state in the $D0_{22}$ ordered structure, at $c=0.25$, as is observed experimentally. Note that considering only first and second neighbors yields an (incorrect) LI_2 ordered structure. However, because the antiphase boundary energy ξ introduced by Kanamori,[17] crosses 0 at approximately $c \sim 0.25$, see Fig. 1, we expect a short-range order of LI_2 type to be superimposed on the long-range order of $D0_{22}$ type. This breakdown of the mean-field theory has been recently demonstrated[18] both theoretically and experimentally for the alloy Pd_3V.

Furthermore, although the experimental alloy phase diagram of PdV indicates a solid solution around $c=0.5$, recent experiments[19] show the existence of a $B19$ ordered structure, as in PtV, which is a monoclinic distortion of LI_0. This type of ordering, without distortion, is also predicted by our calculations summarized in Table I. At the same time, as $V_2^{(2)}$ increases around $c=0.75$ (where a stable $A15$ is expected), LI_0 can still be formed as a metastable state. Finally, around $c=\frac{1}{9}$ we expect an ordered structure of Ni_8Nb type to be stable,[20] although kinetic considerations may prevent the formation of such an ordered state. It should be pointed out that the examination of the most probable ordered structures at $T=0$ K can only be complete through the inclusion of the disordered energy. This, in turn, requires the proper treatment of the $l=3$ terms in the multiple-scattering expressions of the total energy in the KKR CPA. Work along these lines is currently under way.

Figure 2 clearly indicates the rapid convergence of the effective pair interactions as a function of distance, at $c=0.5$, for both PdV and PdRh alloys. In contrast to PdV, all pair-wise interactions for PdRh are negative, indicating strong tendencies toward phase separation at $T=0$ K. This is certainly consistent with the existence of a miscibility gap in the entire range of concentration of the PdRh alloy phase diagram.

Our results demonstrate that the GPM, used in conjunction with a first-principles KKR CPA formalism, constitutes a viable and computationally feasible approach to the calculation of phase stability in binary substitionally disordered alloys. Before accurate quantitative answers can be obtained, further work is necessary in order to incorporate self-consistency in the total energy, exchange and correlation effects, elastic interactions, and lattice relaxation into the theory of alloy phase stability.

One of us (P.E.A.T.) acknowledges helpful discussions with Dr. F. Ducastelle and Professor F. Gautier. The work of A. G. was partly supported by the U.S. Department of Energy under Grant No. DE-FG02-84 ER45 with Northwestern University. The work of G. M. S., W. H. B., and D. M. N. was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

[*] Permanent address: Metals and Ceramics Division, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, TN 37831.

[1] R. Kikuchi, Phys. Rev. **81**, 998 (1951); J. M. Sanchez, F. Ducastelle, and D. Gratias, Physica A **128**, 334 (1984); D. de Fontaine, Solid State Phys. **34**, 73 (1979).

[2] K. Binder, J. L. Lebowitz, M. H. Phani, and M. H. Kalos, Acta Metall. **29**, 1655 (1981); K. Binder, in *Festkörperprobleme: Advances in Solid State Physics,* edited by P. Grosse (Vieweg, Braunschweig, 1986), Vol. XXVI.

[3] V. Heine and D. Weaire, Solid State Phys. **24**, 249 (1970).

[4] J. W. D. Connolly and A. R. Williams, Phys. Rev. B **27**, 5169 (1983).

[5] B. L. Gyorffy and G. M. Stocks, Phys. Rev. Lett. **50**, 374 (1983).

[6] A. Gonis, X. G. Zhang, A. J. Freeman, P. Turchi, G. M. Stocks, and D. M. Nicholson, Phys. Rev. B **36**, 4630 (1987).

[7] F. Ducastelle and F. Gautier, J. Phys. F **6**, 2039 (1976).

[8] A. Bieber and F. Gautier, Acta Metall. **34**, 2291 (1986), and references therein.

[9] C. Sigli, M. Kosugi, and J. M. Sanchez, Phys. Rev. Lett. **57**, 253 (1986); P. Turchi, M. Sluiter, and D. de Fontaine, Phys. Rev. B **36**, 3161 (1987); B. P. Turchi, M. Sluiter, Z. Fu, and D. de Fontaine (to be published).

[10] J. S. Faulkner, in *Progress in Materials Science,* edited by J. W. Christian, P. Hassen, and T. B. Massalski (Pergamon, New York, 1982), Vol. 27, No. 1 and No. 2, and references therein.

[11] B. L. Gyorffy and M. J. Stott, in *Band Structure Spectroscopy of Metals and Alloys,* edited by D. J. Fabian and L. M. Watson (Academic, New York, 1973), p. 385. The index c refers to quantities calculated in the frameork of the CPA.

[12] J. S. Faulkner and G. M. Stocks, Phys. Rev. B **21**, 3222 (1980).

[13] W. H. Butler, Phys. Rev. B **31**, 3260 (1985).

[14] D. D. Johnson, D. M. Nicholson, F. J. Pinski, B. L. Gyorffy, and G. M. Stocks, Phys. Rev. Lett. **56**, 2088 (1986).

[15] B. L. Gyorffy and G. M. Stocks, J. Phys. (Paris) Colloq. **35**, C4-75 (1974).

[16] D. D. Johnson, F. J. Pinski, and G. M. Stocks, Phys Rev. B **30**, 5508 (1984).

[17] J. Kanamori and Y. Kakehashi, J. Phys. (Paris) Colloq. **38**, C7-274 (1977).

[18] F. Solal, R. Caudron, F. Ducastelle, A. Finel, and A. Loiseau, Phys. Rev. Lett. **58**, 2245 (1987).

[19] R. Kuntzler (private communication).

[20] A. J. Ardell and K. Janghorban, in *Phase Transformations During Irradiation,* edited by F. V. Nolfi, Jr. (Applied Science, New York and London, 1983), Chap 9.