PHYSICAL REVIEW B VOLUME 41, NUMBER 14 15 MAY 1990-I

Total-energy and pressure calculations for random substitutional alloys

D. D. Johnson
Sandia National Laboratories, P.O. Box 969, Livermore, California 94551-0969

D. M. Nicholson
Metals and Ceramics Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6114

F. J. Pinski
Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221

B. L. Györffy
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Royal Fort, Bristol BS8 1TL, United Kingdom

G. M. Stocks
Metals and Ceramics Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6114

(Received 28 December 1989)

We present the details and the derivation of density-functional-based expressions for the total energy and pressure for random substitutional alloys (RSA) using the Korringa-Kohn-Rostoker Green's-function approach in combination with the coherent-potential approximation (CPA) to treat the configurational averaging. This includes algebraic cancellation of various electronic core contributions to the total energy and pressure, as in ordered-solid muffin-tin-potential calculations. Thus, within the CPA, total-energy and pressure calculations for RSA have the same foundation and have been found to have the same accuracy as those obtained in similar calculations for ordered solids. Results of our calculations for the impurity formation energy, and for the bulk moduli, the lattice parameters, and the energy of mixing as a function of concentration in fcc $\mathrm{Cu}_c\mathrm{Zn}_{1-c}$ alloys show that this generalized density-functional theory will be useful in studying alloy phase stability.

I. INTRODUCTION

Most commercially useful alloys are complex multiphase mixtures containing ordered and disordered phases. Thus, an understanding of alloy phase stability in terms of first-principles, microscopic theory is not only of academic interest but a matter of practical importance in modern alloy-design efforts. Although much effort in electronic-structure theory is oriented toward understanding the energetics of ordered solids from parameter-free, microscopic methods, this effort provides information of only a few possible points in a typical phase diagram. Also, these ordered-phase calculations give invaluable insight, but they cannot provide a general understanding of phase stability without a concomitant theory for treating the various disordered solid-solution phases.

In recent years it has become clear that Hohenberg-Kohn-Sham density-functional theory (DFT) in the local approximation[1,2] (LDFT) provides a sound theoretical basis for calculating the ground-state properties of pure metals[3] and ordered compounds.[4] Consequently, LDFT provides a logical starting point for a general theory of alloy phase stability, provided that it can be extended to the tractable calculation the energetics of disordered solid solutions.

To this end, we present LDFT-based expressions for calculating the total energy and pressure of random substitutional alloys. These expressions rely on the charge self-consistent Korringa-Kohn-Rostoker coherent-potential approximation (KKR-CPA) for calculating the electronic structure of random alloys.[5] To exhibit their usefulness in studying alloy energetics, we present results for α-phase $\mathrm{Cu}_c\mathrm{Zn}_{1-c}$ random alloys for the equilibrium lattice spacings, the bulk moduli, and the heats of mixing as a function of the copper concentration (c), and also the unrelaxed zinc impurity formation energy in copper.

In order not to obscure the subtleties and approximations involved, in Secs. II–VI we detail the various steps necessary to obtain generalized density-functional-theory expressions for random solid solutions within the muffin-tin KKR-CPA. Section II deals with LDFT and its limitations in the alloy problem. Section III addresses the problem of configurationally averaging the total energy. The use of the CPA to obtain a configurationally averaged total-energy expression is outlined in Sec. IV. The local-density-functional theory for disordered alloys is presented in Sec. V. This section also includes the derivation of the pressure expression for disordered alloys. At the same time, mathematical details are relegated to the Appendixes in order not to obscure the logical development of the formalism. In Sec. VI, the numerical details of the calculations are given. In Sec. VII we present the results of our calculations and in Sec. VIII we present a summary of our work.

II. DENSITY-FUNCTIONAL THEORY

Density-functional theory is based on the Hohenberg-Kohn theorem[1] which states that the total energy $E[\rho(\mathbf{r})]$ is a unique functional of the electron density $\rho(\mathbf{r})$, and that $E[\rho(\mathbf{r})]$ is a minimum for the true ground-state $\rho_0(\mathbf{r})$. The minimization condition (with the number of particles in the system constrained) yields a single-particle Euler's equation which allows one to obtain $\rho(\mathbf{r})$ by solving, self-consistently, a set of single-particle Schrödinger-like equations.

In LDFT the effective potential $v(\mathbf{r})$ entering the Schrödinger equation (or Kohn-Sham equations) is local; furthermore, for ordered systems, $v(\mathbf{r})$ is periodic. Taken together these properties allow use of modern high-speed band-structure-theory algorithms to solve the single-particle equations. For systems without long-range order, such as random substitutional alloys (RSA), two major obstacles render an exact treatment of the LDFT equations intractable. Firstly, the effective potential $v(\mathbf{r};\{\zeta_i\})$ is not periodic, since it depends on the alloy configuration specified by the set of random site-occupation variables ζ_i (e.g., for an *A*-*B* binary alloy ζ_i is 1 or 0 if the site *i* is occupied by atom *A* or *B*). This configurational dependence alone makes a direct solution of Schrödinger's equation impossible. Secondly, experimentally one measures configurationally averaged properties. Consequently, comparison of the calculated energy of formation, for example to experimental data, requires the calculation of the configurationally averaged energy $\bar{E}$ given by

$$\bar{E}=\sum_{\{\zeta_i\}} P(\{\zeta_i\})E[\rho(\mathbf{r};\{\zeta_i\})] \ , \tag{1}$$

where $E[\rho(\mathbf{r};\{\zeta_i\})]$ is the total LDFT energy in a configuration specified by $\{\zeta_i\}$, $P(\{\zeta_i\})$ is the probability of occurrence of a given configuration, and the summation is over all possible configurations compatible with the given concentration. Note that $P(\{\zeta_i\})$ for an ideal solid solution binary alloy would be a binomial distribution. Although the applicability of LDFT has not been altered by the loss of translational symmetry, an alternate route for solution must be found, because the large number of possible configurations makes a direct calculation unfeasible.

III. THERMODYNAMIC IDENTITY

The energy $E[\rho]$ is a known functional of the electronic charge density, except for the exchange and correlation contributions. One way to compute the configurationally averaged energy $\bar{E}$ embodied in Eq. (1) is to average the expression for $E[\rho]$ in some approximation. For example, the Hartree contribution to $\bar{E}$ requires the average of a product of charge densities, and hence Green's functions. Given our use of the CPA which only obtains the average of a single Green's function directly, how does one approximate this average product? How does one estimate the errors involved, and are systematic improvements possible? It is not clear how to answer these question directly. Our goal in this paper is to produce a generalized LDFT expression for $\bar{E}[\rho]$, within the muffin-tin approximation, which resolves these problems.

The pathway to a solution is provided by recourse to quantum statistical mechanics within the grand-canonical ensemble. For a statistical system in equilibrium (at fixed temperature and volume), the thermodynamic identity,

$$-\left[\frac{\partial\Omega(T,V,\mu)}{\partial\mu}\right]_{T,V}=\mathcal{N}(\mu) \ , \tag{2}$$

equates the number of electrons, $\mathcal{N}(\mu)$, to the partial derivative of the thermodynamic grand potential Ω with respect to the chemical potential μ.[6] Noting that

$$\mathcal{N}(\mu)=\int_{-\infty}^{+\infty} d\varepsilon\, n(\varepsilon)f(\varepsilon-\mu) \ , \tag{3}$$

where $f(\varepsilon-\mu)$ is the Fermi function and $n(\varepsilon)$ is the density of states, we may integrate Eq. (2) to obtain $\Omega(T,V,\mu)$ at constant temperature and volume. By taking the zero-temperature limit, averaging over all configurations, and using the functional chain rule,[7] we obtain the fundamental equation for the configurationally averaged ground-state energy, i.e.,

$$\begin{aligned}\bar{E}_e-\mu\mathcal{N}(\mu)=&-\int_{-\infty}^{+\infty} d\varepsilon\, \bar{N}(\varepsilon;\mu)\Theta(\mu-\varepsilon)\\ &+\int_{-\infty}^{\mu} d\mu' \int_{-\infty}^{\infty} d\varepsilon\, \Theta(\mu'-\varepsilon)\frac{d\bar{N}(\varepsilon;\mu')}{d\mu'} \ ,\end{aligned} \tag{4}$$

where $\bar{N}$ denotes the configurationally averaged integrated density of states per site (at constant temperature and volume) and Θ is the unit-step function. We note that the first term is the usual single-particle contribution, and the second term is the so-called double-counting contribution. Also, be aware that $\bar{E}_e$ contains only the contributions of the electrons in an external potential. It does not yet include the energy of the ion-ion interactions; when these interactions are combined with $\bar{E}_e$, it will become the total energy $\bar{E}$ of the system.

Several comments on Eq. (4) are noteworthy. Firstly, as it stands, it is an exact expression for the electronic energy of both ordered (see Appendix A) and disordered systems. Usually, however, some approximation is made for $\bar{N}$, which may make the calculation of $\bar{E}$ tractable, albeit approximate. Secondly, $\bar{N}$, and therefore $\bar{E}$, is related to the average of a single Green's function within LDA. Thus, within LDA we eliminate the need to construct explicitly an approximation to an average of a product of Green's functions, which resolves the questions that arose in connection with our previous discussion of the average of the Hartree terms. (In general, recall that the many-body Green's functions are dependent upon all higher-order Green's-function products.) Thirdly, to obtain a generalized DFT, one then only requires a density-functional-theory-based approximation to $\bar{N}$ for the disordered alloy. Finally, within the KKR-CPA an approximation to $\bar{N}$ exists and it has been used in many studies of the electronic structure of random substitutional alloys.[5]

IV. THE KRR-CPA METHOD

A. Overview

The modern *ab initio* theory of the electronic structure of random alloys is based on the KKR-CPA method.[5] The method is currently based on a Hamiltonian which consists of a random array of nonoverlapping, muffin-tin potentials $v_\alpha(\mathbf{r}-\mathbf{R}_i)$ centered on the lattice sites $\mathbf{R}_i$, with as many different kinds of potentials as there are atomic species α. The essence of the CPA is to approximate, on the average, the scattering properties of a random array of real muffin-tin wells v_α, described by its single-site scattering matrices t_α, by the scattering properties of an ordered array of effective scatterers, each described by a single-site scattering t_c matrix. The scattering properties of this CPA "effective medium" are then determined self-consistently from the requirement that an electron traveling in an infinite array of these effective scatterers does not, on the average, scatter when a single t_c is replaced by a t_α. This CPA condition leads to the best single-site or mean-field theory describing disordered systems. Once the scattering properties of a single t_c are known, quantities such as the averaged integrated density of states (DOS) $\bar{N}(\varepsilon)$, site-restricted average density of states $\bar{n}_\alpha(\varepsilon)$, and charge densities $\bar{\rho}_\alpha(\mathbf{r})$ can be calculated.[5] The partial averaged, single-site charge density $\rho_{\alpha,i}$, for example, is defined to be the single-site charge density at a site i, when the site i is occupied by the species α, and the average is taken over all possible environments. In the rest of this paper, such restricted averages will be denoted as single-site averages and will be discussed further in the derivation of the kinetic energy given in Appendix C.

B. Charge self-consistency

The self-consistent KKR-CPA method makes the single-site electron densities $\bar{\rho}_\alpha(\mathbf{r})$ consistent with the potentials $v_\alpha(\mathbf{r})$.[8,9] In keeping with the single-site nature of the CPA, $v_\alpha(\mathbf{r}-\mathbf{R}_i;\{\zeta_i\})$ is assumed to be independent of configuration, i.e., equal to $v_\alpha(\mathbf{r}-\mathbf{R}_i;\zeta_i)$, which depends only on the occupancy of the site i and the average concentration. Henceforth we denote this potential as $v_\alpha(\mathbf{r}-\mathbf{R}_i)$. In metallic alloys, this is not such a drastic approximation because of the local nature of the impurity screening. The potential $v_\alpha(\mathbf{r}-\mathbf{R}_i)$ is regarded as being an appropriate single-site averaged potential. It is obtained by associating with each site i the nuclear density $Z_\alpha\delta(\mathbf{r}-\mathbf{R}_i)$ and an electronic charge density

$$\rho_\alpha(\mathbf{r}-\mathbf{R}_i)=\begin{cases}\bar{\rho}_\alpha(r), & r\le R_{\mathrm{MT}}\\ \bar{\rho}_0, & R_{\mathrm{MT}}<r<\text{unit-cell boundary}\ ,\end{cases} \tag{5}$$

where R_{MT} is the radius of the muffin-tin sphere and the constant $\bar{\rho}_0$ is the average electron density in the interstitial region. In addition, for the purpose of calculating the total energy and reconstructing the single-site potentials, the average nuclear and electronic densities associated with the site i, i.e., $\bar{Z}\delta(\mathbf{r}-\mathbf{R}_j)=\sum_\alpha c_\alpha Z_\alpha\delta(\mathbf{r}-\mathbf{R}_j)$ and $\bar{\rho}(\mathbf{r}-\mathbf{R}_j)=\sum_\alpha c_\alpha\rho_\alpha(\mathbf{r}-\mathbf{R}_j)$, are placed on all sites $j\neq i$. Charge neutrality requires

$$\bar{Z}_0=\bar{\rho}_0\Omega_0=\bar{Z}-4\pi\int_0^{R_{\mathrm{MT}}}dr\,r^2\sum_\alpha c_\alpha\rho_\alpha(\mathbf{r})\ , \tag{6}$$

where $\Omega_0=\Omega-4\pi R_{\mathrm{MT}}^3/3$ is the interstitial volume, and Ω is the volume of the unit cell. We specify the potentials for the muffin-tin approximation to be

$$\begin{aligned}v_\alpha(\mathbf{r})=&\frac{-2Z_\alpha}{r}+8\pi\int_0^r ds\,s^2\left[\frac{1}{r}-\frac{1}{s}\right]\bar{\rho}_\alpha(s)\\&+8\pi\int_0^{R_{\mathrm{MT}}}ds\,s\bar{\rho}_\alpha(s)+\mu_{\mathrm{xc}}(r;\bar{\rho}_\alpha)\\&-\mu_{\mathrm{xc}}(r;\bar{\rho}_0)+\frac{C\bar{Z}_0}{a}\ ,\end{aligned} \tag{7}$$

where C is a constant that depends on the crystal structure,[10] a is the lattice spacing, and μ_{xc} is the LDFT exchange-correlation potential. This choice for the single-site potential and its corresponding zero gives $v(r)$ in Eq. (7) the usual form in the pure limits, and, as we shall see in a later section, leads explicitly to the variational nature of the total energy.

Note, other implementations of the charge-neutrality condition, Eq. (6), are possible. For example, we could require the individual cell to be charge neutral. Such a choice is clearly unphysical since no charge transfer would be possible. We have constructed the potentials [Eq. (7)] as if the charge located in the interstitial for all species is the same, i.e., the average interstitial charges. This simplifies the form of the potentials and is the simplest choice that would allow a properly variational total energy to be obtained within the muffin-tin approximation (see Sec. V B). However, if the interstitial charges from different species α differ significantly, we have improperly described a portion of the Coulomb energy involving the interstitial region. Essentially, we have ignored our initial choice of dividing up space and assigning the charge within that space. With $\bar{\rho}_\alpha^0$ defined as the interstitial electron density in a cell occupied by a species α, the correction to the present description of the Coulomb energy that must be included for more general applications is

$$\begin{aligned}\Delta U_{\mathrm{Coul}}=&\sum_\alpha c_\alpha[(\overline{\rho_\alpha^0})^2-(\overline{\rho_0})^2]\int_{\Omega_0}d\mathbf{r}'\,|\mathbf{r}-\mathbf{r}'|^{-1}\\&+\sum_\alpha c_\alpha[(Z_\alpha-\overline{\rho_\alpha^0}\Omega_0)(\overline{\rho_\alpha^0}-\overline{\rho_0})]\int_{\Omega_0}d\mathbf{r}'\,|\mathbf{r}'|^{-1}\ .\end{aligned}$$

In most transition-metal alloys and in the Cu-Zn system that we will report on here, the interstitial charge densities for each species differ by less than 0.05 electron, and the missing Coulomb energy contribution is negligible. Thus, for the present we will proceed within the framework of Eq. (6). We will return to the effect of the above Coulomb correction in a later publication.

The above self-consistent KKR-CPA method has been applied to a number of alloy systems with considerable success.[9,11] These results, taken together with the results of earlier, non-self-consistent calculations, lead to the conclusion that the method may be of sufficient accuracy to allow for the calculation of total energies, etc. However, an important difficulty with the method is that the self-consistency step (and, therefore, the variational step in LDFT) and the configurational-averaging step are inextricably mixed together. Consequently, until the introduction of the CPA, it had not been possible to begin with the LDFT equations for the configurational average of the total energy and to derive a set of equations that in a single-site approximation would require *only* the single-site charge densities. It is the advantage of the thermodynamic relation that we only require $\bar{N}(\varepsilon;\mu)$ to determine $\bar{E}$, and, within the KKR-CPA, $\bar{N}$ is the one salient quantity obtained.[12] The intertwined nature of the configurational averaging and the charge self-consistency is implicit in $\bar{N}$ through the potentials. This means that from $\bar{N}$ (which is obtained via the KKR-CPA set of self-consistency equations) we are able to derive the corresponding expression for the configurationally averaged total energy which is DFT-based and charge self-consistent.

V. GENERALIZED DENSITY-FUNCTIONAL THEORY

A. Total energy

Before presenting a rigorous derivation of the muffin-tin total energy, we give an intuitive feeling for what should be expected. In Appendix A, we show that the usual total-energy expression for a system [Eq. (A8)] can be obtained via the Green's function and for ordered systems gives the expected form. If one uses this functional form for the energy of the disordered state and follows the basic assumptions of the single-site CPA (i.e., v_α's are configuration independent, averages are performed with respect to a single site, and the scattering of the effective medium is determined only after concentration averaging), then one can arrive at a proper expression for the alloy total energy (with no muffin-tin approximations). Another procedure for obtaining the same expression for the electrostatic energy is to place the charge densities ρ_α and potentials v_α (both with their full angular dependence) at the site i, their concentration weighted values (e.g., $\bar{\rho}$) on all other sites, and evaluating the integrals over all space. For the band-energy contribution, one could use the partial densities of states for each species, appropriately averaged.

Immediately two concerns about these approaches come to mind. Firstly, the band energy terms may not be correct for the alloy (a proper definition of the kinetic energy is necessary); secondly, the energy may no longer be properly variational (required for various properties within LDA). Notably, the results from a formal derivation from the KKR-CPA equations are unchanged from these intuitive ways of proceeding, which attests to the underlying beauty of the CPA in its description of configurational averaging in disordered systems.

Since the solution of the KKR equations for ordered potentials with no shape approximations is still under development and it is computationally much more demanding, we initially chose to use the muffin-tin approximation to the energy. This method of solution has been in use for many years. The well-known results of Moruzzi, Janak, and Williams[3] (henceforth MJW) attest to its usefulness. In this case, the CPA equations are simple to solve, and, thereby, make the muffin-tin KKR-CPA method a worthwhile pursuit. However, it should be noted that even though the muffin-tin approximation simplifies greatly the solution of the KKR-CPA method, it does produce certain problems due to its unphysical description of the system. For example, the variational nature of the total energy is difficult to ensure in the muffin-tin approximation.

It is the purpose of this section to derive carefully the KKR-CPA alloy total energy within the muffin-tin approximation. From the details given here, the results for potentials without shape approximations may be determined straightforwardly.

To evaluate the general result for a configurationally averaged total energy [Eq. (4)], it is necessary to have some expression for the total number of particles (in this case, electrons) in the system. The integrated density of states, $\bar{N}(\varepsilon;\mu)$, is related to the total number of electrons via Eq. (3), and, within the KKR-CPA, is given by the generalized Lloyd formula[12]

$$\bar{N}(\varepsilon;\mu)=N_0(\varepsilon)-\pi^{-1}\mathrm{Im}[\ln\det|t_c^{-1}(\varepsilon)-g(\varepsilon)|]$$
$$+\sum_\alpha c_\alpha \ln\det|1+[t_\alpha^{-1}(\varepsilon)-t_c^{-1}(\varepsilon)]\tau_c(\varepsilon)|\ , \qquad (8)$$

where t_α and t_c are t matrices which describe the scattering properties of scatterers of type α and the CPA effective scatterer, respectively, g is the real-space structure-constant matrix, τ_c is the site-diagonal part of the total scattering path operator for an ordered lattice of effective scatterers,[13] and N_0 is the free-electron contribution. Note, that in this equation, matrices have indices in both the angular-momentum variable $L=(l,m)$ and the site index n, and $\det(\cdots)$ denotes a determinant. Making use of this equation, we recast the electronic total energy for the muffin-tin CPA, Eq. (4), in the form

$$\bar{E}_e-\mu\bar{N}(\mu)=-\int_{-\infty}^{\infty}d\varepsilon\,\bar{N}(\varepsilon;\mu)\Theta(\mu-\varepsilon)-\int_0^{R_{\mathrm{MT}}}d\mathbf{r}'\sum_\alpha c_\alpha\bar{\rho}_\alpha(\mathbf{r}')v_\alpha(\mathbf{r}')$$
$$+\int_{-\infty}^{\infty}d\mu'\int_0^{R_{\mathrm{MT}}}d\mathbf{r}'\,\Theta(\mu-\mu')\sum_\alpha c_\alpha v_\alpha(\mathbf{r}')\frac{d\bar{\rho}_\alpha(\mathbf{r}')}{d\mu'}\ , \qquad (9)$$

where the $\mathbf{r}$-space integrals are over a single unit cell. Both ρ_α and v_α depend on μ', since μ' controls the band filling. The derivation of Eq. (9) is given in Appendix B. With use of integration by parts, another useful form is obtained:

$$\bar{E}_e=\mu\bar{N}(\mu)-\int_{-\infty}^{\infty}d\varepsilon(\varepsilon-\mu)\sum_\alpha c_\alpha\bar{n}_\alpha(\varepsilon)-\int_0^{R_{\rm MT}}d\mathbf{r}'\sum_\alpha c_\alpha\bar{\rho}_\alpha(\mathbf{r}')v_\alpha(\mathbf{r}')$$

$$+\int_{-\infty}^{\infty}d\mu'\int_0^{R_{\rm MT}}d\mathbf{r}'\,\Theta(\mu-\mu')\sum_\alpha c_\alpha v_\alpha(\mathbf{r}')\frac{d\bar{\rho}_\alpha(\mathbf{r}')}{d\mu}\ . \tag{10}$$

As shown in Appendix C, the first three terms of Eq. (10) give the configurationally averaged kinetic energy $\bar{T}$. Adding the ion-ion Coulomb energy to the last term, the configurationally averaged potential energy and exchange-correlation energy $\bar{U}=U_{\rm Hartree}+E_{\rm xc}$ is obtained. Within the muffin-tin approximation it can be written as

$$\bar{U}=-8\pi\sum_\alpha c_\alpha\left[Z_\alpha\int_0^{R_{\rm MT}}ds\,s\bar{\rho}_\alpha(s)-4\pi\int_0^{R_{\rm MT}}ds\,s\bar{\rho}_\alpha(s)\int_0^s dr'r'^2\bar{\rho}_\alpha(r')\right]$$

$$-\frac{C\bar{Z}_0^2}{2a}+4\pi\int_0^{R_{\rm MT}}dr\,r^2\sum_\alpha c_\alpha\bar{\rho}_\alpha(r)\varepsilon_{\rm xc}[\bar{\rho}_\alpha]+\Omega_0E_{\rm xc}[\bar{\rho}_0]\ , \tag{11}$$

where $E_{\rm xc}$ ($\varepsilon_{\rm xc}$) is the exchange-correlation energy (density), and the last two terms give its contribution to the total energy.

In this derivation of the muffin-tin CPA energy, we have made a similar muffin-tin approximation to that of Janak in his derivation[14] of the energy functional for an ordered system. As is perhaps not surprising, the energy may be written as

$$\bar{E}=\sum_\alpha c_\alpha E_J[\bar{\rho}_\alpha,\bar{\rho}_0;\bar{n}_\alpha]\ , \tag{12}$$

where E_J is an expression of the same form as that obtained by Janak [see Eq. (25) of Ref. (14)] except that the pure-metal muffin-tin and interstitial charge densities $\rho(r)$ and ρ_0 are replaced by $\bar{\rho}_\alpha(r)$ and $\bar{\rho}_0$, and that the density of states is calculated within the KKR-CPA.

Equation (12) is an appealing result for several reasons. Firstly, once a self-consistent KKR-CPA calculation has been performed, an accurate evaluation of the total energy is straightforward. In addition, all of the subtle single-particle and double-counting cancellations in Janak's original formulation apply, i.e., the large electronic core contributions may be algebraically canceled. This endows the calculation of the alloy total energies with the same precision usually encountered in the calculations of ordered systems. Secondly, this equation is valid for any number of components. Thirdly, in the pure metal limit, Eq. (12) reduces to Janak's expression. Finally, the simple form of the CPA total-energy expression is primarily due to the fact that $\bar{N}(\varepsilon)$ is stationary with respect to variations of the CPA scattering matrices[15] t_c^{-1}. Therefore, no *explicit* dependence on the CPA scattering matrices is obtained (see Appendix B). For other approximations to the configurational averaging, such as the Korringa average-*t*-matrix approximation (ATA), this may not be the case and the ensuring simplification would not follow. Thus, it is the mean-field potential construction method embodied in Eq. (7) and the mean-field CPA condition for determining t_c, etc., that have together produced a result with a large number of desirable properties.

B. Variational nature

The energy functional constructed in usual DFT has the property that the first variation of $E[\rho]$ about the ground-state charge density vanishes[1] subject to the condition that $\int d\mathbf{r}\,\rho(\mathbf{r})=N$, i.e., $\delta\{E[\rho]-\mu N\}/\delta\rho_\alpha(\mathbf{r})=0$. This property establishes the charge self-consistency procedure since it implies $\delta U[\rho]/\delta\rho_\alpha(\mathbf{r})=c_\alpha v_\alpha(\mathbf{r})$. In other words, variationally one may obtain a single-particle Schrödinger's equation and the effective potential necessary to calculate $\rho(\mathbf{r})$ and, therefore, $E[\rho]$. In the disordered alloy, once the CPA has been used, it is not clear how to apply the standard DFT and therefore we have taken a different approach. We have determined the functional form of the alloy total energy by constructing an effective potential compatible with the CPA assumptions. We now show that the theory has a stationarity property and therefore establishes a self-consistency procedure for disordered alloys. Recall that the potential, although compatible with the CPA assumptions, was constructed by *ad hoc* method. We have already given some possible alternatives regarding the interstitial electron density. In addition, there is some arbitrariness in the choice of the interstitial exchange-correlation potential. For example, it could have been chosen for a binary *A*-*B* alloy as $c_A\mu_{\rm xc}[\bar{\rho}_A^0]+c_B\mu_{\rm xc}[\bar{\rho}_B^0]$, instead of $\mu_{\rm xc}[\bar{\rho}_0]$, where $\bar{\rho}_0$, $\bar{\rho}_A^0$, and $\bar{\rho}_B^0$ are the average interstitial charge density and interstitial charge densities on a site *A* and *B*, respectively. Unless the expression for the muffin-tin $\bar{E}$ is carefully constructed, the variation of $\bar{E}$ with respect to $\bar{\rho}_\alpha(\mathbf{r})$ does not necessarily vanish.

It is straightforward to show from Eq. (11) that indeed $\delta\bar{U}[\rho]/\delta\bar{\rho}_\alpha(\mathbf{r})=c_\alpha v_\alpha(\mathbf{r})$. Similarly, from Appendix D, it is true that $\delta\bar{T}[\rho]/\delta\bar{\rho}_\alpha(\mathbf{r})=-c_\alpha v_\alpha(\mathbf{r})$. It is then obvious that

$$\delta\{\bar{E}[\rho]-\mu\bar{N}\}/\delta\bar{\rho}_\alpha(\mathbf{r})=0\ , \tag{13}$$

where $\bar{E}$ corresponds to an extremum for a given solution, $\{\bar{\rho}_\alpha\}$, to the effective single-particle Schrödinger equations. We note in passing that the potential obtained by variation of the kinetic energy is the same potential obtained via the variation of the potential energy only for the true ground-state electron density. In a self-consistent calculation care must be taken to maintain this variational property of the energy. We give more details of this in Sec. VI. Thus, the theory is self-consistent in analogy to usual DFT.

C. Pressure

Even though the pressure may be obtained by numerical differentiation of the calculated total energy with respect to lattice spacing, there are good reasons for obtaining expressions that allow direct computation of the pressure from the results of a self-consistent field calculation at a single lattice spacing. As was pointed out by Janak,[14] there are also numerical advantages in calculating the pressure which are associated with the algebraic cancellation of large contributions from the core states. Furthermore, obtaining consistency between the pressure calculated directly and by numerical differentiation of the total-energy curve provides a stringent test of the numerical implementation of the whole self-consistent total-energy formalism.

In what follows, we cannot simply use the derivations of Slater[16] or Janak[14] as a basis for finding the expression for the pressure in the case of a disordered random alloy. Those derivations relied on manipulations of wave functions. Within the CPA, the average "wave function" is not defined. This forces an alternative approach. We relegate the details to Appendix E and only sketch the approach below.

Consider $\{\mathbf{R}_n\}$ to be the lattice for which we are to calculate the pressure and denote the energy for this lattice to be $\bar{E}_0$. As the lattice is contracted to $\{(\mathbf{R}_n/\lambda)\}$ by a scaling factor λ, the energy changes from $\bar{E}_0$ to $\bar{E}^\lambda$. Clearly, the pressure is given by the derivative of the energy with respect to λ, evaluated at $\lambda=1$:

$$\bar{P}=-\left.\frac{d\bar{E}}{d\Omega}\right|_{\Omega=\Omega_0}=\left.\frac{1}{3\Omega_0}\frac{d\bar{E}}{d\lambda}\right|_{\lambda=1}, \tag{14}$$

where Ω_0 is the volume at $\lambda=1$. From this expression, it is evident that if the energy scales with λ in a simple fashion, then the pressure may be calculated concomitantly with the energy.[17-19]

The λ dependence of $\bar{E}^\lambda$ is investigated in Appendix E, where its various contributions, i.e., kinetic, electrostatic, and exchange-correlation energies, are found to behave similarly to their counterparts in ordered LDA energy expressions. The derivative in Eq. (14) can be formally evaluated and a pressure expression results that can be written as a straightforward generalization of Janak's expression for ordered systems, i.e.,

$$\bar{P}=\sum_\alpha c_\alpha P_J[\bar{\rho}_\alpha,\bar{\rho}_0;\bar{n}_\alpha]\ , \tag{15}$$

where P_J is Janak's expression for the pressure,[14] excepting that the average site-restricted density of states, $\bar{n}_\alpha$, and the electron densities obtained from a self-consistent KKR-CPA calculation are to be used.

D. Discussion

Several specific comments on the preceding section are in order. (i) In the muffin-tin approximation our particular choice of the interstitial exchange-correlation potential is necessary in order to obtain certain cancellations leading to Eq. (13), and hence a variational expression for the alloy energy. (ii) Performing the variation with respect to the single-site charge densities $\bar{\rho}_\alpha$, and not, say, $\bar{\rho}=\sum_\alpha c_\alpha\bar{\rho}_\alpha$, is in accord with the CPA, in that the site-restricted averages exist for each species separately, and hence may be varied independently. (iii) It is not necessary to separate $\bar{E}$ into kinetic- and potential-energy contributions,[7] but having done so, one can take advantage of the algebraic cancellations of the large electronic core contributions. (iv) This theory is straightforward to generalize for multisublattice crystal structures, or to magnetic alloys (using the local-spin-density approximation[20]). (v) Although derived for the muffin-tin Hamiltonian, the theory is straightforwardly applicable to the atomic-sphere approximation (ASA). (vi) If the KKR method were to be generalized to the case of nonspherical scatterers, this theory could be easily extended to include this generalization. (vii) Since the theory is a mean-field theory of the electronic structure and is readily extendable to finite temperatures, it fits logically into a theory of alloy concentration fluctuations,[21] in which the entropy contributions are also treated within a mean-field approximation. Finally, the strength of the formulation given in this appear lies in the internal consistency of its components, i.e., the CPA, the muffin-tin potential, the total energy, and the pressure.

VI. NUMERICAL CONSIDERATIONS

Our implementation of the theory presented in this paper relies on a number of numerical details which lead to stable and precise results. Therefore, before we provide an example of its application, we include, for completeness' sake, a description of those numerical details. In addition, the major approximations made in the solution of the KKR-CPA equations (beyond the assumed muffin tins) are stated.

Because of the analytic properties of the KKR-CPA theory,[22] use was made of contour integration in the complex energy plane. That is, the calculations, and therefore the integrals over energy [such as those required for calculating the band energies (involving densities of states) and charge conservation (involving Green's functions)], were performed in the complex energy plane,[23,24] using a rectangular contour. Typically, only 120–150 energies around the contour are required to obtain convergence of the total energy and charge density. The bottom of the contour was perpendicular to the real energy axis and was located typically 0.3–0.4 Ry below the muffin-tin zero. The long side of the contour ran parallel to the real axis and about 0.8 Ry away. The top of the contour again ran perpendicular to the real energy axis and intersected it at the Fermi energy (ε_F). On the first two legs of the contour the real-space formulation[8] of the CPA equations was used. Typically our implementation of the real-space method[25] includes only the multiple-scattering contributions to the fifth-nearest-neighbor shells; nonetheless, the solution along these two portions of the contour is essentially exact due to the large damping of the scattered waves produced when the imaginary part of the energy is relatively large.

On the final portion of the contour we used the momentum-space formulation. The necessary Brillouin-zone integrals are performed using a directional prism method.[26] At imaginary energies of 0.8 Ry, or greater, the real-space and the momentum-space solution of the multiple-scattering equations match to a precision of 1 part in 10^5, hence our choice of contour and method of solution around the contour. In the concentrated alloys, we have found that 10 directions in the reduced $\frac{1}{48}$th of the Brillouin zone were sufficient to yield an uncertainty in the total energy of 0.1 mRy. Using 36 directions, we obtained an order-of-magnitude improvement in the precision. For the dilute alloys and the pure elements, it was necessary to use 136 directions to arrive at a **k**-converged total energy, since the absence of disorder and its associated smearing increases the sharpness of states. Along each direction we evaluated the Brillouin-zone integrand using 20–50 points, with the number of points adjusted to increase as the real axis was approached. Each element of the inverse of the KKR determinant in the integrand (i.e., $\tau_c(\varepsilon)=\Omega_{\rm BZ}^{-1}\int d\mathbf{k}\,[t_c^{-1}(\varepsilon)-g(\varepsilon)]^{-1}$) was split into a cofactor and a determinant. Along a particular **k** direction, a cubic interpolation is used for both the cofactor and the determinant. Within an interval, the integral was obtained from an analytic expression evaluated with coefficients obtained from the cubic interpolation. Thus, along a given direction the contribution to the integral is determined accurately; as indicated earlier, however, care must be taken with the angular dependence of the integrand, hence the large number of directions for the pure elements. The procedure outlined above works well as long as some broadening of states exists, either from disorder or because the energy has at least a small imaginary part.

A further important numerical feature involves the solution of the CPA equations. Far off in the complex plane only a few nearest-neighbor shells contribute to the solution. In fact, as $\mathrm{Im}(\varepsilon)\rightarrow\infty$ it is physically intuitive and easy to show rigorously that the CPA equations are solved by the average-t-matrix approximation (ATA). In this case, no iterations of the CPA equations are necessary. Even when $\mathrm{Im}\varepsilon$ is a few hundredths of rydbergs, only 1–2 iterations of the CPA self-consistency equations are necessary to obtain an accurate solution. On the real axis, 10–16 iterations may be necessary when the Fermi energy lies within the d bands. Thus, performing the calculation over a contour in the complex ε plane minimizes the number of iterations necessary to solve the CPA equations. A further consideration is that several equivalent forms of the CPA equations are possible. However, we have found one form[27] to be particularly useful since it is related to a Newton-Raphson numerical-integration procedure, yet requires no evaluation of the derivatives of the τ_c matrices (which are costly). We have found in all instances investigated thus far that iterating this equation, starting always with the ATA, yields only the physically relevant solution of the CPA throughout the complex energy plane, including the real energy axis. We have also incorporated a convergence accelerator in its solution, such as that used in converging charge densities in the charge self-consistency step, which can, in some instances, reduce by a factor of 2 the number of necessary iterations. Derivations and further details of this CPA equation are given in Ref. 27.

In calculating the t matrices and Green's functions, etc., we have truncated the angular-momentum sums at $l_{\rm max}=3$ (f symmetry). Our predominant interest to date has been the third- and fourth-row transition-metal alloys. The contributions from higher-order angular-momentum components to these quantities should be small. The effect of this approximation will be briefly discussed in Sec. VII. For the exchange-correlation potential, we have used the von Barth–Hedin functional form, as parametrized by Moruzzi, Janak, and Williams.[3]

Furthermore, one must be careful in the handling of the core electron densities. For the evaluation of the energy and pressure, it is important to use the subtle algebraic cancellation of terms involving the core contributions affected in Janak's[14] original muffin-tin formulas. These cancellations are exact only when the core charge density vanishes at the muffin-tin radius, a condition which is not met by shallow bound states. Consequently, we have combined the electron density from these weakly bound states (or "semicores") within the valence density, and designate only the charge from deeply bound states as "core." Having made this designation, we evaluate the energy and pressure using the functional forms derived earlier, which incorporate the aforementioned cancellations. For some elements, such as palladium, failing to properly define the core states can give rise to a 10–100-mRy error in the total energy.

The final detail of note, which was not discussed in Janak's original formulation for ordered systems, is the inclusion of terms to make the total energy stationary during the self-consistency cycle. This stationarity results from the evaluation of the expectation value of the underlying Hamiltonian. In a self-consistent-field (SCF) iteration cycle, care must be taken to maintain the integrity of this expectation value. In particular, the output electron densities ($v_{\rm out}$) must be used to construct the electrostatic energy and the input potentials ($v_{\rm in}$) must be used to calculate the kinetic energy. In Janak's formulation, the algebraic cancellations of the core contributions do not preserve this property and two terms must be added to ensure stationarity of the energy, namely, $\int d\mathbf{r}\,\rho_{\rm core}(v_{\rm out}-v_{\rm in})$ and $\int d\mathbf{r}\,r\rho_{\rm core}d(v_{\rm out}-v_{\rm in})/dr$. Clearly, at convergence these terms are zero, as suggested in the discussion of the variational property of the alloy total energy, Sec. V B.

VII. RESULTS

For both historical and pedagogical reasons we have chosen the fcc Cu-Zn alloys to demonstrate the general features of this density-functional approach to the energetics of disordered alloys. Although stable fcc Cu-Zn (α phase) alloys exist only in a limited range of Zn concentrations (0–38 at. % Zn), metastable fcc alloys exist up to 55 at. % Zn. From a pedagogical viewpoint, the Cu-Zn system exhibits most of the troublesome features that are found in more complex alloy systems and that are the driving force for some of the technical developments described in the preceding section. In the following subsections, we show results for the fcc equilibrium lattice constants, bulk moduli, and energies of formation (enthalpies) as a function of concentration, and the *unrelaxed* Zn impurity formation energy in pure Cu.

A. Equilibrium lattice constants

The equilibrium lattice constant (or volume) is among the quantities which are least sensitive to numerical details, e.g., angular-momentum truncation and spherical approximation to the potentials. Typical agreement between theory and experiment for pure elements and compounds is 0.5–3 %, the larger error applying to magnetic systems where the spin-polarization effects are described less accurately by the exchange-correlation functions used. As we have pointed out earlier, there are two means of obtaining the equilibrium lattice constant: either from the minimum in the energy or from zero pressure. There is typically a small difference between these lattice constants in all methods, whether based on full or spherical potentials; the pressure method usually results in a smaller lattice constant by about 0.5%.

In Fig. 1, we show the energy versus lattice constant for the fcc $\mathrm{Cu}_{0.5}\mathrm{Zn}_{0.5}$ alloy. These results are typical of fcc Cu-Zn alloys. The lattice constant obtained via the energy is $a_E = 6.962$ a.u., and is within 0.5% of the experimental value. On the other hand, the pressure curve (Mbar), see Fig. 2, yields $a_P = 6.933$ a.u., which is 0.5% smaller than a_E. To note the general trend of error, we find for pure Cu that $a_E = 6.765$ a.u., whereas from experiment one finds $a_{\mathrm{expt}} = 6.809$ a.u. at $T = 0$ K; the difference is less than 0.7%. From the pressure curve, we find that $a_P = 6.743$ a.u.; this may also be compared to a calculation by Moruzzi, Janak, and Williams[3] for pure Cu, which gave a lattice constant of $a = 6.767$ a.u. from a similar muffin-tin KKR calculation but with $L_{\max} = 4$ truncation. Thus, equilibrium lattice constants for the disordered alloys are seen to be determined with accuracy similar to calculations for ordered alloys, i.e., within 0.5–3 % of experimental values.

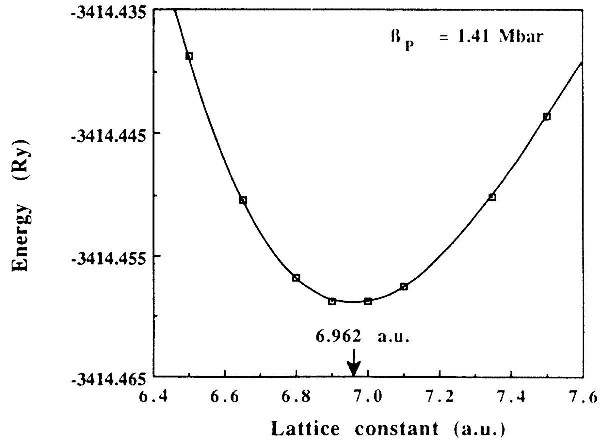

FIG. 1. The variation of the alloy total energy (Ry) with lattice constant (a.u.) for fcc $\mathrm{Cu}_{0.50}\mathrm{Zn}_{0.50}$ alloy. A cubic least-squares fit gives a minimum energy of -3414.45888 Ry at 6.962 a.u. and a bulk moduli of 1.41 Mbar. This plot is typical for the fcc CuZn alloys.

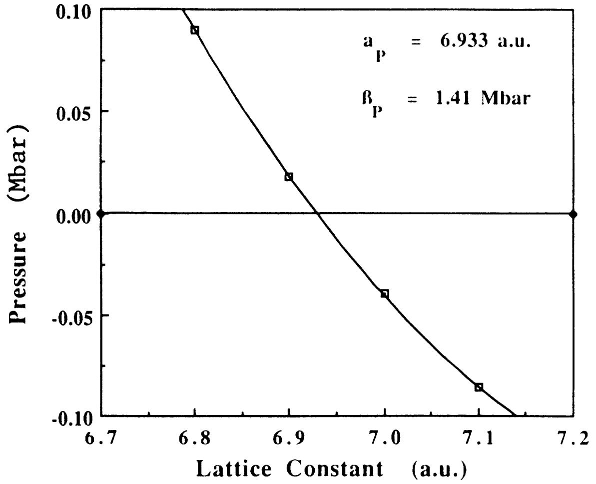

FIG. 2. The variation of the alloy pressure (Ry) with lattice constant (a.u.) for fcc $\mathrm{Cu}_{0.50}\mathrm{Zn}_{0.50}$ alloy. The zero of pressure is found at 6.933 a.u., along with a bulk moduli of 1.41 Mbar.

The equilibrium lattice constants were determined via a cubic, least-squares fit to the energies calculated at (typically) five lattice constants. Figure 3 shows the variation of the calculated lattice constant with concentration. The salient feature is the deviation from Vegard's rule[28] (linear variation of the lattice constant with concentration for the same Bravais lattice). The deviation from Vegard's rule experimentally observed in α-phase alloys is given correctly by the theory. The variation of the lattice constant upon addition of Zn to Cu, in the dilute limit, is found to be $\partial a/\partial c|_{c=0} = 0.0036$/at. % Zn, whereas the Vegard's rule obtained from our calculated lattice constants is 0.0052/at. % Zn. This is to be compared with the experimental value of 0.003 66±7/at. % Zn near

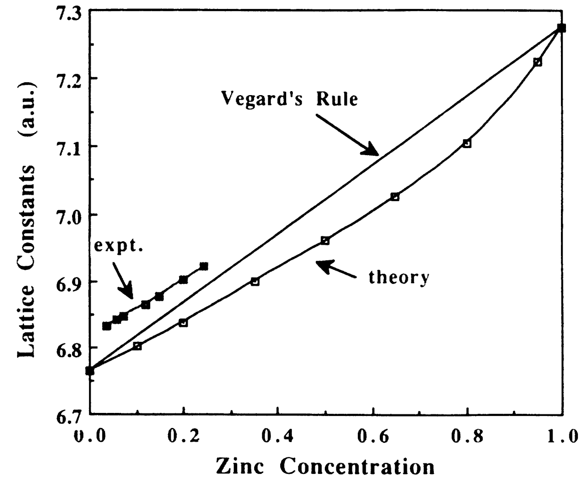

FIG. 3. Concentration variation of the lattice constant (a.u.) for the fcc CuZn alloys.

300 K. The experimental value and its error were obtained from a least-squares fit to the compiled data between 0% and 15% zinc.[29,30] We note that the comparison has been made between experiments at 300 K and zero temperature calculations. The difference between 300- and 0-K lattice constants for pure Cu is $\Delta a = -0.010$ a.u. (about -0.15%).[29,30] This small shift should be approximately the same for the dilute alloys as well, so the value $\partial a/\partial c|_{c=0}$ at $T=0$ K should differ little from the value at 300 K.

B. Bulk moduli

The bulk modulus (β) of each system may be determined straightforwardly from either the curvature of the energy or the slope of the pressure, a function of lattice constant. As noted in the text, the pressure is more sensitive to the convergence of the charge density because, unlike the total energy, it is not variational with respect to the charge density. We therefore obtained the bulk moduli via the curvature of the energy. The bulk moduli obtained from the pressure are usually within a few percent of the energy results. For example, the bulk moduli is 1.41 Mbar from both methods for the 50% alloy; however, for pure copper, $\beta = 1.67$ and 1.70 Mbar from the energy and pressure, respectively. In Fig. 4, we show the concentration dependence of the bulk modulus, in the fcc phase. The line is only a guide to the eye. We note that not all of the bulk moduli were determined with as many points as the pure elements or the 50% alloy; therefore the relative error across the concentration range is about 0.05 Mbar.

Usually density-functional calculations for ordered metals yield bulk moduli that are 10–20 % in error. This also is the case for these disordered alloy calculations. For example, experimentally for pure copper $\beta = 1.42$ Mbar, whereas we obtain from the energy $\beta_E = 1.67$ Mbar (an 18% error), or $\beta_P = 1.68$ Mbar from the pressure. The MJW result of 1.55 Mbar (a 9% error) via the pressure is closer to experiment. This difference in the theoretical results is not significant since both are within the typical error. For the 50/50 alloy, the $\beta_E = 1.41$ Mbar at $a = 6.962$ a.u. ($\beta_P = 1.41$ Mbar at $a = 6.933$ a.u.) Essentially, our results for the bulk moduli show a rigid shift from the fcc ($T=0$ K) experimental values, indicating that trends should be believable. For most other pure elements that we have tested, our calculations agree well with those of Moruzzi, Janak, and Williams.

As pointed out by MJW,[3] the bulk modulus is determined primarily by the interstitial electron density, i.e., the most loosely bound electrons. The difference between our theoretical bulk moduli of pure elements and that of MJW results from a greater number (0.016) of interstitial electrons in our calculations. This discrepancy, from two very similar calculations, probably results from a number of effects. (i) The states which we have defined as core levels; that is, we (properly) define a core level to be that which has a wave function that is zero at the muffin-tin radius, otherwise the charge density from a shallow bound state is combined with the valence charge density. On the other hand, in their original calculations MJW renormalized the small amount of charge outside the muffin tin due to the upper-lying core to be inside the muffin-tin radius. However, we have performed, as a check, a similar renormalization within our code and obtain only a 0.003 reduction in interstitial electrons for copper. (ii) We truncate our angular-momentum sums at $l_{\max} = 3$, whereas MJW truncated at $l_{\max} = 4$. In hindsight, this is probably the major source of the discrepancy because elements that have just filled a d shell of electrons, such as copper, could easily have a small amount of charge relocated to within the muffin-tin sphere with the increase in variational freedom created from including more angular-momentum components. (iii) The numerical methods used within each code are very different and could also result in a small difference in charge arrangement.

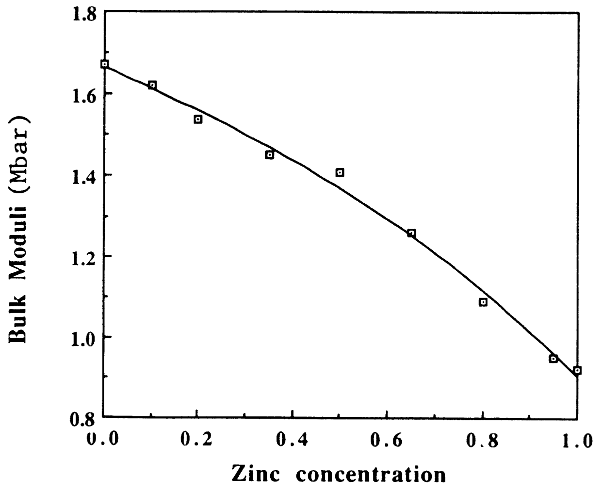

FIG. 4. Concentration variation of the bulk moduli (Mbar) for the fcc CuZn alloys. Although the trend is given properly, there is the usual 10–20 % error compared to experiment.

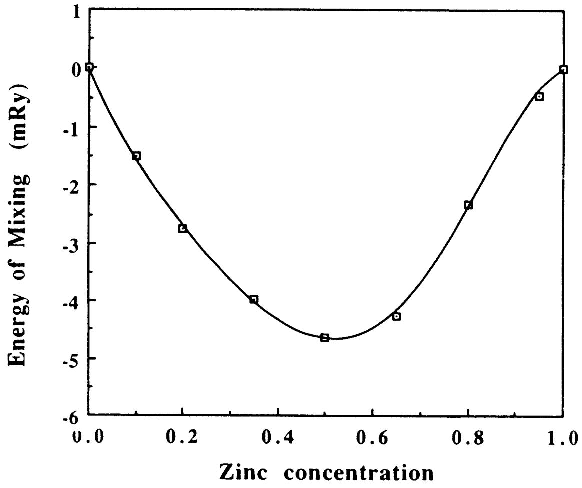

FIG. 5. Concentration variation of the heats of mixing (m Ry) for fcc CuZn.

Regardless of the explanation, the requirement of charge neutrality [Eq. (6)] places a small amount of core charge in the interstitial region, which is then distributed equally throughout this volume, increasing β. In fact, from the behavior of the bulk moduli versus r_s $[r_s \equiv (4\pi\rho/3)^{-1/3}]$ (see β versus r_s plot on page 14 of Ref. 3), it is easy to show that our 1.67-Mbar result will be reduced to 1.55 Mbar by reducing the interstitial electron number by 0.016. Although this does not explain the origin of the difference, it does show a consistency between the two calculations.

It is interesting to observe that, quite generally within LDA calculations, if one evaluates the curvature of the calculated energy versus volume curve not at the theoretical volume but at the experimental volume, one obtains bulk moduli within a few percent of the experimental values. This suggests that the curvature of the energy versus volume curve obtained theoretically is rather accurate, only slightly rotated so as to give a smaller volume.

C. Energy of mixing

The energies of mixing (ΔE^{mix}), or formation enthalpies, are important for determining phase stability. Obviously, for use in addressing materials questions, the accuracy of the calculated energies is important. In this paper we show the fcc energies of formation of $\text{Cu}_c\text{Zn}_{1-c}$. We leave a calculation of the relative stability of phases (e.g., fcc and bcc) to a future paper.

In Fig. 5, we have plotted the concentration variation of the energies of mixing for fcc Cu-Zn alloys. It should be noted that the curve is not parabolic. This deviation from the parabolic form will be especially important when comparing the energetics of different crystallographic phases. The calculated formation energy for the random solid solution is smaller in magnitude than the experimental value. For example, at $c=35\%$, $\Delta E^{\text{mix}}=-4.05$ mRy, with experiment giving -6.0 ± 0.5 mRy.[30,31] Experimentally,[31] it is known that substantial short-range order exists. The affect of this is to lower the formation energy. This is perhaps obvious since the phase diagram of Cu-Zn shows the $B2$ phase is metastable at relatively low temperatures (and about 1.3 mRy more favorable than the bcc disordered state[31]), while near $T=0$ K the $L1_0$ phase becomes stable.

As mentioned, in these calculations we are investigating the totally random solid solution (without short-range order), which, strictly, exists only at "infinite" temperatures. Thus, we should not expect agreement with experiment. For a direct comparison to experiment, either the effects of short-range order should be subtracted from the experimental results (if possible), or the effects of short-range order added to the theory. The latter possibility can be investigated within the theory of concentration fluctuations[21] or of the generalized perturbation method.[32]

D. Impurity formation energy

In dilute alloys, the impurity formation energy (ΔE^{imp}) is an important quantity for determining solubilities. If we neglect charge redistribution on neighboring atoms and local lattice relaxations, then the CPA is exact in the single-impurity limit.[33] Thus, our calculations provide a means of obtaining this quantity. In fcc alloys, local relaxation effects account typically for less than 0.1 eV ($\approx$7.4 mRy), particularly if the constituent atoms are similar in size. (bcc alloys usually have much larger relaxation effects than fcc alloys since their local environments are less isotropic than the fcc alloys.) As an example of this type of calculation, we have investigated the Zn impurity formation energy in fcc Cu, and compared it to experiment.

The impurity formation energy of Zn in Cu is given by

$$\Delta E^{\text{imp}} = \left. \frac{d(\Delta E^{\text{mix}})}{dc_{\text{Zn}}} \right|_{c_{\text{Zn}}=0} , \tag{16}$$

where we take the concentration derivative of the energy of mixing at the pure-Cu limit. One could evaluate at each concentration the energy versus lattice constant, minimize the energy, fit the minimum energies, and then take the numerical derivative. However, the most straightforward means to obtain this quantity is to calculate ΔE^{mix} for small concentrations with the volume *fixed* at the calculated equilibrium volume of the pure element. Obviously, the first method would increase the number of calculations required and introduces more error into the calculation of ΔE^{imp}. Note, one requires the energies for the two pure elements in order to calculate the energy of mixing. These energies should be obtained for their respective equilibrium lattice constants.

We have performed such calculations at $c_{\text{Zn}}=2\%$, 6%, and, 10% at the volume of pure Cu and obtain the energies -3281.31352, -3292.40919, and -3303.50477 Ry, respectively. For the pure elements, the energies were $E_{\text{Cu}}=-3275.76569$ Ry and $E_{\text{Zn}}=-3553.14290$ Ry. Thus, the energies of mixing were 0.0, -0.32, -0.87, and -1.36 mRy for 0%, 2%, 6%, and 10%, respectively. A cubic, least-squares fit to these numbers yields $\Delta E^{\text{imp}}=-17$ mRy (-0.231 eV). Dederichs *et al.*[34] have calculated the Zn impurity formation energy in Cu via an impurity Green's-function method in which the impurity energy is calculated directly (with or without local relaxation). They obtained -0.26 eV without and -0.33 eV with local relaxation. Experimentally, ΔE^{imp} is in the range of -0.24 to -0.40 eV from Kubaschewski *et al.*[35] and -0.23 to -0.34 eV from Hultgren *et al.*[30] The spread in values depends on whether one looks at enthalpies of mixing or partial molar enthalpies; the experimental error[30,35] quoted for the enthalpies of mixing is about 0.05 eV. Thus, both sets of calculations lie within the experimental range. Typically, the experimental error is 10–20 %, since there are various experimental methods, adiabatic or isothermal, to extract the impurity formation energies from enthalpies or enthalpy derivatives; also, the experimental values do reflect the possible short-range order of the alloys, because a range of concentrations is required to extract this quantity. The overall agreement between ΔE^{imp} from a proper impurity calculation and the limit of an alloy calculation is rather remarkable. For small concentrations of Zn, the impurity formation energies are, as shown above, a few hundredths of rydbergs at most, which means that to compare to experiment the energies of mixing are needed to an accuracy of better than 0.01 mRy, since it is the derivative that is desired. For this particular quantity, our internal consistency and relative accuracy is of great importance.

VIII. SUMMARY

As a step toward understanding general alloy phase stability, we have presented a theory of the energetics of metallic alloys which is equally applicable to ordered and disordered phases. The results given here are particular to the muffin-tin implementation of the KKR-CPA. But, as we have suggested, the theory carries through for potentials which involve no shape approximations. As such, it will be applicable, at least in principle, to nonmetallic disordered systems. The theory is applicable to an arbitrary number of components and it is easily extendable to magnetic systems and systems in which it is useful to consider multiple sublattices. Although we have only considered a fcc random solid solution here, this first implementation of this theory of alloy energetics of the disordered binary Cu-Zn gives us considerable confidence towards applying it to more general problems. For fcc $\mathrm{Cu}_c\mathrm{Zn}_{1-c}$ alloys, the theory provides quantitatively accurate results for lattice constant, bulk moduli, and energetics, i.e., mixing and impurity energies.

ACKNOWLEDGMENTS

We acknowledge useful discussions with W. H. Butler, J. S. Faulkner, and A. Gonis. We also thank W. Wolfer and A. Gonis for a critical reading of the manuscript. One of us (F.J.P.) acknowledges the generous support of the Ohio Supercomputer Center. Crucial computing support was supplied by the Pittsburgh Supercomputing Center to two of us (F.J.P. and D.D.J.) G.M.S. acknowledges the continued computational support by the U.S. Department of Energy (DOE) Energy Fusion Supercomputing Program through the National Magnetic Fusion Energy Computer Center (Livermore, CA). Some of this work was performed while D.D.J. received partial support from National Research Council and U.S. Naval Research Laboratory. This work has been supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, at Sandia National Laboratories and at Oak Ridge National Laboratory (under Contract No. DE-AC05-84-1400 with Martin Marietta Energy Systems, Inc.),

APPENDIX A

In this Appendix, we derive from the Green's function the fundamental expression for the total energy, Eq. (4), which yields, as expected, the usual results for ordered elements. For simplicity, we deal only with the ground-state ($T=0$ K) case. Let $E_e-\mu N=E_1+E_2$, where E_1 is the single-particle contribution and E_2 is the double-counting corrections [see the discussion following Eq. (4)]. The single-particle term can be partially integrated and written as

$$E_1=\int_{-\infty}^{\infty} d\varepsilon(\varepsilon-\mu)n(\varepsilon)\Theta(\mu-\varepsilon) \tag{A1}$$

which will be used later. The double-counting term, E_2, may be directly related to changes of the potential with respect to the chemical potential by the chain rule. This manipulation is worthwhile because the potential directly governs the scattering properties of the system, affecting $N(\varepsilon)$, and also the total energy is usually expressed as a function at $\rho_\alpha(\mathbf{r})$ and $v_\alpha[\mathbf{r};\rho_\alpha(\mathbf{r})]$. Thus, by the chain rule,

$$\frac{dN(\varepsilon;\mu)}{d\mu}=\int_{-\infty}^{\infty} d\mathbf{r}\frac{\delta N(\varepsilon;\mu)}{\delta v(r)}\frac{dv(\mathbf{r})}{d\mu}\ , \tag{A2}$$

where N is the integrated density of states for the system. The change in $N(\varepsilon)$ due to the change in $v(r)$ can be found starting from the definition of $\delta N(\varepsilon)$ which can be written as

$$\delta N(\varepsilon)=-\pi^{-1}\,\mathrm{Im}\int_{-\infty}^{\infty} d\varepsilon' \int d\mathbf{r}\,\delta G(\mathbf{r},\mathbf{r};\varepsilon')\Theta(\mu-\varepsilon')\ . \tag{A3}$$

Quite generally, $\underline{G}=\underline{G}_0+\underline{G}_0\underline{v}\,\underline{G}$ (using matrix notation) which yields $\delta\underline{G}=\underline{G}\,\delta\underline{v}\,\underline{G}$, where $\underline{G}_0$ is the free-space Green's function. Using the closure property, i.e., $\int d^3\mathbf{r}\,|\mathbf{r}\rangle\langle\mathbf{r}|=1$, and $dG/d\varepsilon=-G^2$, it is easily shown that

$$\delta N(\varepsilon)/\delta v(\mathbf{r})=\pi^{-1}G(\mathbf{r},\mathbf{r};\varepsilon)\ . \tag{A4}$$

Combining Eqs. (A2) and (A4), we obtain

$$E_2=\pi^{-1}\,\mathrm{Im}\int_{-\infty}^{\mu} d\mu' \int_{-\infty}^{+\infty} d\varepsilon \int d\mathbf{r}\,G(\mathbf{r},\mathbf{r};\varepsilon)\times\Theta(\varepsilon-\mu')\frac{dv(\mathbf{r})}{d\mu'}\ . \tag{A5}$$

By performing the energy integral over ε and partially integrating with respect to μ', it follows that

$$E_2=-\int d\mathbf{r}\,\rho(\mathbf{r})v[\rho(\mathbf{r})]+\int_{-\infty}^{\infty} d\mu' \int d\mathbf{r}\,v[\rho(\mathbf{r})]\frac{d\rho(\mathbf{r})}{d\mu'}\ . \tag{A6}$$

With the exchange-correlation potential given as $\delta E_{\mathrm{xc}}/\delta\rho(r)=\mu_{\mathrm{xc}}(r)$, the potential is

$$v(\mathbf{r})=v^{\mathrm{ext}}(\mathbf{r})+2\int d\mathbf{r}'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\mu_{\mathrm{xc}}(\mathbf{r})\ , \tag{A7}$$

where $v^{\mathrm{ext}}(\mathbf{r})=\sum_{\{\mathbf{R}\}}-2Z_R/|\mathbf{r}-\mathbf{R}|$ is the electron-ion potential, and $\{\mathbf{R}\}$ denotes the ion positions.

By integrating over μ' and including the ion-ion contribution, the total energy, $E=E_1+E_2+E_{\text{ion-ion}}$, for an arbitrary arrangement of atoms forming a charge-neutral system is

$$\begin{aligned}E={}&\mu N+\int_{-\infty}^{\infty} d\varepsilon(\varepsilon-\mu)n(\varepsilon)\Theta(\varepsilon-\mu)-\int d\mathbf{r}\,\rho(\mathbf{r})v(\mathbf{r})\\&+\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\rho(\mathbf{r})\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-2\sum_{\{\mathbf{R}\}}Z_R\int d\mathbf{r}\frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{R}|}\\&+\sum_{\substack{\{\mathbf{R},\mathbf{R}'\}\\(\mathbf{R}\neq\mathbf{R}')}}\frac{Z_RZ_{R'}}{|\mathbf{R}-\mathbf{R}'|}+E_{\mathrm{xc}}[\rho]\ .\end{aligned} \tag{A8}$$

When all the unit cells are equivalent, Eq. (A8) is the usual expression for the total energy for an ordered system. As usual, the single-particle kinetic energy is given by the first three terms, the last term is the exchange-correlation contribution, and the remaining terms comprise the potential energy of the system.

APPENDIX B

Here we derive the functional form of the configurationally averaged total energy within the CPA in terms of eigenvalue sums, potentials, and charge densities. We begin with our fundamental equation for the total energy, Eq. (4) in the text. Since $N(\varepsilon;\mu)$ depends on μ only through the scattering matrices $\underline{t}_c^{-1}$ and $\underline{t}_\alpha^{-1}$, it follows that

$$\frac{\delta\bar{N}}{\delta\mu'}=\mathrm{tr}\left[\frac{\delta\bar{N}}{\delta t_c^{-1}}\frac{\partial t_c^{-1}}{\partial\mu'}+\sum_\alpha\frac{\delta\bar{N}}{\delta t_\alpha^{-1}}\frac{\partial t_\alpha^{-1}}{\partial\mu'}\right], \tag{B1}$$

where the trace (tr) is taken with respect to the angular-momentum index $L=(l,m)$ and site index n. Due to the property of the CPA that N is stationary[15] with respect to variations in $\underline{t}_c^{-1}$, the first term in Eq. (B1) vanishes. Thus, the expressions derived will have no explicit dependence on the coherent potential v_c. Since the scattering properties are determined by the potentials, we use the chain rule to expand Eq. (B1) to give

$$\frac{\delta\bar{N}}{\delta\mu'}=\mathrm{tr}\left[\sum_\alpha\frac{\delta\bar{N}}{\delta t_\alpha^{-1}}\int d\mathbf{r}\frac{\delta t_\alpha^{-1}}{\delta v_\alpha(\mathbf{r})}\frac{\partial v_\alpha(\mathbf{r})}{\partial\mu'}\right]. \tag{B2}$$

Furthermore, for real spherically symmetric scatterers, the variation of the single-site scattering matrices due to changes in the local potential is given by

$$\frac{\delta t_\alpha^{-1}(\varepsilon)}{\delta v_\alpha(\mathbf{r})}=-Z_L^\alpha(\mathbf{r},\varepsilon)Z_L^\alpha(r,\varepsilon) \tag{B3}$$

with $Z_L(r;\varepsilon)=z_l(r;\varepsilon)Y_{lm}(\hat{\mathbf{r}})$, $z_1(r;\varepsilon)$ is the regular solution to the radial Schrödinger equation at energy ε, and $Y_{lm}(\hat{\mathbf{r}})$ is a real spherical harmonic.[36] (There is of course an appropriate definition of this variation for the non-spherically symmetric scatterer which then could be used to obtain the general non-muffin-tin result.) Using the relation $\ln(\det\underline{A})=\mathrm{tr}(\ln\underline{A})$ and the expression for the integrated density of states within the KKR-CPA, Eq. (8), one finds

$$\frac{\delta\bar{N}}{\delta t_\alpha^{-1}}=-\pi^{-1}\underline{D}_\alpha\underline{\tau}_c\ , \tag{B4}$$

where $\underline{D}_\alpha=[\underline{1}+(\underline{t}_\alpha^{-1}-\underline{t}_c^{-1})\underline{\tau}_c]^{-1}$, and $\underline{\tau}_c=\Omega_{\mathrm{BZ}}^{-1}\int d\mathbf{k}[\underline{t}_c^{-1}-\underline{g}]^{-1}$. Ω_{BZ} is the Brillouin-zone volume. Also, within the CPA, the alloy Green's function is given by

$$G_{LL'}(\mathbf{r},\mathbf{r}';\varepsilon)=\sum_\alpha c_\alpha[Z_L^\alpha(\mathbf{r},\varepsilon)Z_{L'}^\alpha(\mathbf{r}',\varepsilon)(D_\alpha\tau_c)_{LL'}-\delta_{LL'}Z_L^\alpha(\mathbf{r},\varepsilon)\mathbf{J}_{L'}^\alpha(\mathbf{r}',\varepsilon)]\ . \tag{B5}$$

with $\mathbf{J}_L^\alpha(r;\varepsilon)=j_l(r;\varepsilon)Y_{lm}(\hat{\mathbf{r}})$ and the spherical Bessel functions $j_l(r;\varepsilon)$ are the irregular solution of the radial Schrödinger equation which is singular at the origin.[5(d)] Note that the second term in Eq. (B5) is real for real arguments and therefore does not contribute to the density of states at real energies ε. For our present purposes we will neglect this term.

With the charge density given by the trace of the Green's function, i.e.,

$$\rho(\mathbf{r})=-\pi^{-1}\,\mathrm{Im}\int_{-\infty}^{\mu}d\varepsilon\,G(\mathbf{r},\mathbf{r},\varepsilon) \tag{B6}$$

we may use Eqs. (B2) and (B5) with the initial form for the energy, Eq. (4), and perform the integral over energy. Finally, after a partial integration over $\mathbf{r}$, we obtain the form of the alloy total energy which is in terms of potentials, electron densities, and one-electron sums, Eq. (9) of the text.

APPENDIX C

To be able to separate the total energy into its kinetic- and potential-energy contributions, we make use of the definition of the kinetic energy $T(\varepsilon)$ for a given configuration (in atomic units):

$$T(\varepsilon)=\pi^{-1}\mathrm{Im}\int d\mathbf{r}\lim_{\mathbf{r}'\to\mathbf{r}}[\nabla_{\mathbf{r}}^2\mathrm{tr}G(\mathbf{r},\mathbf{r}';\varepsilon,\{\zeta_\iota\})]\ . \tag{C1}$$

The corresponding Green's function satisfies

$$\left[-\nabla_{\mathbf{r}}^2+\sum_i v_i(\mathbf{r};\{\zeta_i\})-\varepsilon\right]G(\mathbf{r},\mathbf{r}';\varepsilon,\{\zeta_i\})=\delta(\mathbf{r}=\mathbf{r}') \tag{C2}$$

where ε is the energy of interest. With the assumptions used in the text for the potential, namely (i) the effective potentials are spherically symmetric, and (ii) partially averaged for a given configuration, and hence are independent of configuration, we obtain

$$\left[-\nabla_r^2+\sum_i v_i(r;\zeta_i)-\varepsilon\right]G(\mathbf{r},\mathbf{r}';\varepsilon,\{\zeta_i\})=\delta(\mathbf{r}-\mathbf{r}')\ . \tag{C3}$$

Equation (C1) may now be rewritten as

$$T(\varepsilon)=\pi^{-1}\,\mathrm{Im}\int d\mathbf{r}\lim_{\mathbf{r}'\to\mathbf{r}}G(\mathbf{r},\mathbf{r}';\varepsilon,\{\zeta_i\})\left[\sum_i v_i(r;\zeta_i)-\varepsilon\right]. \tag{C4}$$

The limit may be taken and, therefore, we require only the site-diagonal Green's function, which is defined by Eq. (B5).

Because the potentials depend only on the site occupation and are arranged on an ordered Bravais lattice, we may derive an expression for the configurationally averaged kinetic energy within the single-site approximation. This can be accomplished by similar arguments leading to the single-site CPA averages.[5(d)] Since $T(\varepsilon)$ depends only on site-diagonal quantities, it is reasonable to first average over the subset of structures in the ensemble that leave the cell i fixed. Note, also, that upon configurationally averaging, one obtains a translationally invariant system and, therefore, we may replace an average over the system by an average over a cell. Performing this site-restricted average yields

$$\langle T(\varepsilon)\rangle_{i,\alpha} = -\pi^{-1}\int d\mathbf{r}[\varepsilon - v_{i,\alpha}(\mathbf{r};\zeta_i)] \times \langle \mathrm{Im}G(\mathbf{r};\varepsilon,\{\zeta_i\})\rangle_{i,\alpha} , \tag{C5}$$

where $\langle \cdots \rangle_{i,\alpha}$ indicates we have conditionally averaged so that on the site i the potential is known to be v_α, and $\langle T(\varepsilon)\rangle_{i,\alpha}$ is the kinetic energy per cell.

The final step in the process consists of averaging over the possible occupants of site i. We then obtain

$$\langle T(\varepsilon)\rangle = -\pi^{-1}\int_\Omega d\mathbf{r}\sum_\alpha c_\alpha([\varepsilon - v_\alpha(\mathbf{r};\zeta_i)]\langle \mathrm{Im}G(\mathbf{r};\varepsilon,\{\zeta_i\})\rangle_{i,\alpha}) . \tag{C6}$$

We now use the single-site CPA to give the site-restricted average of G, Eq. (B5). Thus, integrating over energy we obtain

$$\bar{T} - \mu\bar{N} = -\int_{-\infty}^{\infty} d\varepsilon(\varepsilon-\mu)\Theta(\mu-\varepsilon)\sum_\alpha c_\alpha \bar{n}_\alpha(\varepsilon) - \int_\Omega d\mathbf{r}'\sum_\alpha c_\alpha v_\alpha(\mathbf{r}')\rho_\alpha(\mathbf{r}') . \tag{C7}$$

Using partial integration over ε, the desired form for the configurationally averaged kinetic energy is obtained, i.e.,

$$\bar{T} - \mu\bar{N} = -\int_{-\infty}^{\infty} d\varepsilon\,\bar{N}(\varepsilon;\mu)\Theta(\mu-\varepsilon) - \int_\Omega d\mathbf{r}\sum_\alpha c_\alpha v_\alpha(\mathbf{r})\rho_\alpha(\mathbf{r}) . \tag{C8}$$

Note that all the approximations used in the derivation are consistent with the KKR-CPA.

APPENDIX D

The first variation of $\bar{T} - \mu\bar{N}$ with respect to the site-restricted, configurationally averaged charge densities $\bar{\rho}_\alpha$ are necessary to establish the stationary property of the total energy and can be obtained by arguments similar to those outlined in Appendix A. Consider the functional form of the kinetic-energy equation (C8), the variation is given by

$$\frac{\delta(T-\mu\bar{N})}{\delta\bar{\rho}_\alpha} = -\int_{-\infty}^{\infty} d\varepsilon\,\Theta(\mu-\varepsilon)\frac{\delta\bar{N}}{\delta\bar{\rho}_\alpha} - c_\alpha v_\alpha(\mathbf{r}) - \int_\Omega d\mathbf{r}\sum_\beta c_\beta\rho_\beta(\mathbf{r})\frac{\delta v_\beta(\mathbf{r})}{\delta\rho_\alpha} . \tag{D1}$$

Since $\delta N/\delta t_c^{-1}=0$ within the CPA, the first term of Eq. (D1) yields

$$-\int_{-\infty}^{\infty} d\varepsilon\,\Theta(\mu-\varepsilon)\frac{\delta\bar{N}}{\delta\bar{\rho}_\alpha} = -\int_{-\infty}^{\infty} d\varepsilon\int_\Omega d\mathbf{r}\sum_\beta \frac{\delta\bar{N}}{\delta t_\beta^{-1}}\frac{\delta t_\beta^{-1}}{\delta v_\beta}\frac{\partial v_\beta(\mathbf{r})}{\partial\bar{\rho}_\alpha} . \tag{D2}$$

Using Eqs. (B3)–(B5) and performing the energy integral, the first and third terms in Eq. (D1) cancel and the result stated in the text is obtained, namely $\delta(\bar{T}-\mu\bar{N})/\delta\bar{\rho}_\alpha = -c_\alpha v_\alpha(\mathbf{r})$. Note, if $\{\bar{T}$ minus the temperature multiplied by the entropy$\}$ replaces $\bar{T}$ and a Fermi factor $f(\varepsilon-\mu)$ replaces the step function $\Theta(\varepsilon-\mu)$, then this derivation is equally valid at nonzero temperatures.

APPENDIX E

In Sec. V C we claimed that the energy behaved in a simple way as the lattice is contracted. Here we discuss this behavior in detail and show how the pressure defined in Eq. (14) is reduced to the convenient form of Eq. (15).

As the lattice parameter is varied, the energy changes for three reasons. First, the energy functional depends explicitly on the nuclear positions through nucleus-nucleus Coulomb repulsion; second, the nuclear positions determine the "external potential" in which the electrons move; and third, the electron density (which minimizes the energy functional) must respond to the changes in the "external potential." The energy of the contracted lattice can be expanded about an approximate electron density,

$$\bar{E}^\lambda = \bar{E}^\lambda(\tilde{\rho}^\lambda_\alpha,\{c_\gamma\}) = \bar{E}^\lambda(\tilde{\rho}^\lambda_\alpha,\{c_\gamma\}) + \int d\mathbf{r}\sum_\alpha c_\alpha\Delta\rho^\lambda_\alpha(\mathbf{r})\frac{\delta\bar{E}^\lambda}{\delta\bar{\rho}^\lambda_\alpha} + O((\Delta\rho^\lambda_\alpha)^2) \tag{E1}$$

where $\bar{\rho}^\lambda_\alpha$ is the self-consistent electron density for the contracted lattice, and $\Delta\rho^\lambda_\alpha = \bar{\rho}^\lambda_\alpha - \tilde{\rho}^\lambda_\alpha$. We chose not to specify $\tilde{\rho}^\lambda_\alpha$ at this point other than to impose the restriction that as λ tends to 1, $\tilde{\rho}^\lambda_\alpha$ goes smoothly to $\bar{\rho}^{\lambda=1}_\alpha$. The second term on the right-hand side of Eq. (E1) vanishes since the energy is stationary, and, by construction, the terms of second order (or higher) in $\Delta\bar{\rho}^\lambda_\alpha$ do not contribute to the pressure. In this way, the stationarity of the energy within the CPA is critical in establishing a pressure formula.

To obtain the pressure, all that remains is to choose $\tilde{\rho}^\lambda_\alpha$ and take the derivative of the energy with respect to λ. For ordered metals, Slater chose to set $\tilde{\rho}^\lambda_\alpha = \bar{\rho}^{\lambda=1}_\alpha$ in deriving the pressure in the $X\alpha$ approximation.[16] Janak followed Slater's approach in generalizing the pressure formula to include arbitrary forms of the exchange-correlation energy.[14] As can be seen in Slater's paper, this leads to complicated algebra when evaluating the kinetic energy. Another drawback of this choice is that the manipulations of the Schrödinger equation explicitly involve wave functions. This is a handicap in the CPA formalism because it is a theory of the configuration averaging of the Green function and does not provide information about the wave function.

Following the early work of Fock[17] and the recent work of Martin,[18] we choose the scaled set of densities $\tilde{\rho}^\lambda_\alpha$ defined by densities,

$$\tilde{\rho}_\alpha^\lambda(r)=\lambda^3\bar{\rho}_\alpha(\lambda r)\ , \tag{E2}$$

i.e., we expand the energy about an electron density which is "shrunk" with the lattice. The factor λ^3 preserves the total number of electrons. We are not concerned about the accuracy with which this reference electron density approximates $\bar{\rho}_\alpha^\lambda$; we are only concerned that $\tilde{\rho}_\alpha^\lambda$ is exact as λ tends to one and that the energy is easily evaluated.[19]

The potential energy is easily evaluated by replacing $\bar{\rho}_\alpha^\lambda$ by $\tilde{\rho}_\alpha^\lambda$ in Eq. (11) and adjusting the limits of integration to R_{MT}/λ. By changing the variable of integration, we find

$$\begin{aligned}\bar{U}(\{\tilde{\rho}_\alpha^\lambda\})=&\lambda\bar{U}_{\mathrm{Hartree}}(\{\bar{\rho}_\alpha\})+\bar{Z}_0\varepsilon_{xc}(\lambda^3\bar{\rho}_0)\\&+\int_0^{R_{\mathrm{MT}}/\lambda}dr\sum_\alpha c_\alpha\bar{\rho}_\alpha(r)\varepsilon_{xc}(\lambda^3\bar{\rho}_\alpha)\end{aligned} \tag{E3}$$

Referring to Eq. (C7), we can write the kinetic energy as

$$\begin{aligned}\bar{T}^\lambda(\{\tilde{\rho}_\gamma^\lambda\})=&\int_{-\infty}^{\mu}d\varepsilon\,\varepsilon n_c(\varepsilon;\{\tilde{\rho}_\gamma^\lambda\})\\&-\int_{\Omega/\lambda^3}d\mathbf{r}\sum_\alpha c_\alpha\tilde{\rho}_\alpha^\lambda(r)v_\alpha[\{\tilde{\rho}_\gamma^\lambda\}]\ .\end{aligned} \tag{E4}$$

Here we must be careful about the meaning of $n_c(\varepsilon,\{\tilde{\rho}_\gamma^\lambda\})$ and $v_\alpha[\{\tilde{\rho}_\gamma^\lambda\}]$. As a preliminary step, consider the kinetic energy in an ordered metal, which can be expressed as

$$T(\rho)=\int_{-\infty}^{\mu}d\varepsilon\,\varepsilon n(\varepsilon;\rho)-\int d\mathbf{r}\,\rho v[\rho]\ , \tag{E5}$$

where the relations

$$(-\nabla_{\mathbf{r}}^2+V[r;\rho]-\varepsilon)G(\mathbf{r},\mathbf{r}';\varepsilon)=\delta(\mathbf{r}-\mathbf{r}')\ , \tag{E6}$$

$$V[\rho]=\sum_i v(\mathbf{r}-\mathbf{R}_i;[\rho(\mathbf{r})]) \tag{E7}$$

and

$$\rho(\mathbf{r})=-\pi^{-1}\mathrm{Im}\int_{-\infty}^{\mu}d\varepsilon\,G(\mathbf{r},\mathbf{r},\varepsilon) \tag{E8}$$

define the potential $v[\rho]$, while the density of states is given by

$$n(\varepsilon;\rho)=-\pi^{-1}\,\mathrm{Im}\int d\mathbf{r}\,G(\mathbf{r},\mathbf{r},\varepsilon)\ . \tag{E9}$$

To use Eq. (E5) for the kinetic energy $T(\rho)$, we must find a potential $v[p]$ which in turn gives a Green function whose imaginary trace is $-\pi\rho$. Only the density of states obtained from this potential can be used in Eq. (E4) to evaluate the kinetic energy.

Within the CPA, there is an additional level of complexity. We need to know how the kinetic energy depends on $\{\tilde{\rho}_\alpha^\lambda\}$ through the density of states (DOS). The DOS itself depends only indirectly on $\{\tilde{\rho}_\alpha^\lambda\}$ through the dependence of v_c on $\{v_\alpha\}$. This seemingly complex dependence of the DOS on $\{\tilde{\rho}_\alpha^\lambda\}$ is simplified greatly by the scaling properties of the CPA equations. If we can find a set of potentials $\{v_\alpha(\mathbf{r})\}$ such that the $-\pi^{-1}\mathrm{Im}\langle G_c\rangle_\alpha=\tilde{\rho}_\alpha$ (note the restricted average), then the appropriate DOS, $n(\varepsilon,\{\tilde{\rho}_\alpha^\lambda\})$, to use in Eq. (E4) to evaluate the kinetic energy is $n_c(\varepsilon)$. We now discuss how such a set of potentials $\{v_\alpha(\mathbf{r})\}$ can be constructed.

Given a set of electron densities, it is difficult, or impossible, to find a $\{v_\alpha(\mathbf{r})\}$ that will generate them via the CPA equation; this is true not only for the CPA but for the Schrödinger equation in general. This is why one usually evaluates the energy by using an electron density found by solving the Schrödinger equation; the generating potential is then available. The resolution of this problem lies in the choice of $\tilde{\rho}_\alpha^\lambda(r)$. For the choice of $\tilde{\rho}_\alpha^\lambda(r)=\lambda^3\bar{\rho}_\alpha(\lambda r)$, the generating potentials are [by scaling of the Schrödinger equation, i.e., Eq. (E6)] easily shown to be $\lambda^2 v_\alpha(\lambda r)+\sum_{i(\neq 0)}v_c(\mathbf{r}-\mathbf{R}_i/\lambda)$, where v_α and v_c are the self-consistent potentials for the uncontracted lattice $\{\mathbf{R}_n\}$.

This simple scaling argument involving the Schrödinger equation is independent of the nature of the potential, and, for example, is valid for complex, energy-dependent, and nonlocal potentials and, in particular, for the coherent potential, v_c, as well as for any v_α embedded in the coherent potential. Also, inspecting the CPA equation, one observes that the coherent potential scales in the same way as the potentials v_α. That is, if $v_c(\mathbf{r})$ is the coherent potential corresponding to $\{v_\alpha\}$, then $\lambda^2 v_c(\lambda\mathbf{r})$ corresponds to $\{\lambda^2 v_\alpha(\lambda\mathbf{r})\}$. Furthermore, $\lambda^2 v_\alpha(\lambda\mathbf{r})$ embedded in a CPA medium obtained from $\lambda^2 v_c(\lambda\mathbf{r})$ has a restricted average electron density $\tilde{\rho}_\alpha^\lambda(\mathbf{r})$. Therefore, the density of states, $n_c(\varepsilon,\{\tilde{\rho}_\alpha^\lambda\})$, as determined from the imaginary part of the trace of the Green's function in the CPA medium $\lambda^2 v_c(\lambda\mathbf{r})$, is the appropriate density of states to use in the evaluation of the kinetic energy, Eq. (E4).

We reiterate the three salient points of the above discussion: both $\{v_\alpha\}$ and v_c scale simply with the appropriate choice of the scaled densities, and it follows that n_c is the required density of states to evaluate the one-electron contributions to the energy. Therefore, the sum of the one-electron eigenvalues, when properly scaled, is

$$\begin{aligned}&\int_{-\infty}^{\mu_\lambda}d\varepsilon\,\varepsilon n_c(\varepsilon,\{\tilde{\rho}_\alpha^\lambda\})\\&\quad=-\pi^{-1}\mathrm{Im}\int_{-\infty}^{\mu_\lambda}d\varepsilon\,\varepsilon\int d\mathbf{r}\,\lambda G(\lambda\mathbf{r},\lambda\mathbf{r};\lambda^{-2}\varepsilon)\ .\end{aligned} \tag{E10}$$

Substituting for $n_c(\varepsilon,\{\tilde{\rho}_\alpha^\lambda\})$, $\tilde{\rho}_\alpha^\lambda$, and v_α in Eq. (E4), the kinetic energy is

$$T(\varepsilon,\{\tilde{\rho}_\alpha^\lambda\})=\lambda^2 T(\varepsilon,\{\bar{\rho}_\alpha\})\ . \tag{E11}$$

The pressure is now readily evaluated from the potential and kinetic energy and pressure relation, i.e., Eqs. (E3), (E11), and (14), respectively, and yields

$$3\bar{P}\Omega_0=2\bar{T}+\bar{U}_{\text{Hartree}} -3\sum_{\alpha} c_\alpha \int_0^{R_{\text{MT}}} d\mathbf{r}\, \bar{\rho}_\alpha[\varepsilon_{\text{xc}}(\bar{\rho}_\alpha)-\mu_{\text{xc}}(\bar{\rho}_\alpha)] -3\bar{Z}_0[\varepsilon_{\text{xc}}(\bar{\rho}_0)-\mu_{\text{xc}}(\bar{\rho}_0)] \tag{E12}$$

which is conveniently written as a sum over species [Eq. (15)], i.e.,

$$\bar{P}=\sum_{\alpha} c_\alpha P_J[\bar{\rho}_\alpha,\bar{\rho}_0;\bar{n}_\alpha] \; , \tag{E13}$$

where P_J is the functional form for the pressure derived by Janak[14] and $\bar{\rho}_\alpha$, $\bar{\rho}_0$, and $\bar{n}_\alpha$ are the configurationally averaged muffin-tin charge densities, interstitial charge densities, and density of states, respectively.

---

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); see also the finite-temperature generalization, N. D. Mermin, Phys. Rev. **137**, A1441 (1965).

[2] For example, L. Hedin, and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971); O. Gunnarson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[3] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[4] A. R. Williams, C. D. Gellat, and V. L. Moruzzi, Phys. Rev. Lett. **44**, 429 (1980).

[5] (a) G. M. Stocks and H. Winter, in *Electronic Structure of Complex Systems,* edited by P. Phariseau and W. M. Temmerman (Plenum, New York, 1985), p. 463; (b) G. M. Stocks, W. M. Temmerman, and B. L. Gyorffy, Phys. Rev. Lett. **41**, 339 (1978); (c) J. S. Faulkner and G. M. Stocks, Phys. Rev. B **23**, 5628 (1981); (d) J. S. Faulkner and G. M. Stocks, Phys. Rev. B **21**, 3222 (1980).

[6] See, for example, K. Huang, *Statistical Mechanics* (Wiley, New York, 1963).

[7] Note, without taking the zero-temperature limit, we would have the finite-temperature grand potential for the disordered alloy, i.e., a generalization of references cited as (1) above.

[8] H. Winter and G. M. Stocks, Phys. Rev. B **27**, 882 (1983); G. M. Stocks and H. Winter, Z. Phys. B **46**, 864 (1982).

[9] D. D. Johnson, D. M. Nicholson, F. J. Pinski, B. L. Gyorffy, and G. M. Stocks, Phys. Rev. Lett. **56**, 2088 (1986); D. D. Johnson, Ph.D. thesis, University of Cincinnati, 1985 (unpublished).

[10] R. A. Coldwell-Horsfall and A. A. Maradudin, J. Math. Phys. (N.Y.) **1**, 395 (1960).

[11] See, for example, hyperfine fields: H. Ebert, H. Winter, B. L. Gyorffy, D. D. Johnson, and F. J. Pinski, Solid State Commun. **64**, 1011 (1987); moments: D. D. Johnson, F. J. Pinski, and J. B. Staunton, Appl. Phys. **61**, 3715 (1987); resistivity: G. M. Stocks and W. H. Butler, Phys. Rev. Lett. **48**, 55 (1982); and x-ray photoelectron spectroscopy (XPS) and photoemission: P. Weightman, P. T. Andrews, G. M. Stocks, and H. Winter, J. Phys. C **16**, L181 (1983).

[12] B. L. Gyorffy and G. M. Stocks, J. Phys. (Paris) **35**, C4-75 (1974); see also Ref. 8, pp. 506 and 507.

[13] B. L. Györffy 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).

[14] J. F. Janak, Phys. Rev. B **9**, 3985 (1974).

[15] P. Lloyd and P. V. Best, J. Phys. C **8**, 3752 (1975).

[16] J. C. Slater, J. Chem. Phys. **57**, 2389 (1972).

[17] V. Fock, Z. Phys. **63**, 855 (1930).

[18] O. H. Nielson and Richard M. Martin, Phys. Rev. B **32**, 3780 (1985).

[19] There are subtitles associated with the application of scaling to density functions. These have been addressed in Mel Levy and John P. Perdew, Phys. Rev. A **32**, 2010 (1985); Mel Levy, Weito Yang, and Robert G. Parr, J. Chem. Phys. **83**, 2334 (1985).

[20] For the spin-polarized version, if the muffin-tin zero is taken with respect to the majority spins, the following charge-neutrality requirements will result in a straightforward generalization of all our equations:

$$\bar{Z}_0^{\uparrow}=\bar{\rho}_0^{\uparrow}\Omega_0=\bar{Z}-\int_{\Omega} d\mathbf{r}\sum_{\alpha} c_\alpha\bar{\rho}_\alpha^{\downarrow}-4\pi\int_0^{R_{\text{MT}}} dr\, r^2\sum_{\alpha} c_\alpha\rho_\alpha^{\uparrow} \; ,$$

$$\bar{Z}_0^{\downarrow}=\bar{\rho}_0^{\downarrow}\Omega_0=\bar{Z}-\int_{\Omega} d\mathbf{r}\sum_{\alpha} c_\alpha\bar{\rho}_\alpha^{\uparrow}-4\pi\int_0^{R_{\text{MT}}} dr\, r^2\sum_{\alpha} c_\alpha\rho_\alpha^{\downarrow} \; ,$$

where ↑ and ↓ refer to the electron spin. Other definitions remain equally valid, however the zero of the potential must be handled carefully.

[21] B. L. Gyorffy and G. M. Stocks, Phys. Rev. Lett. **50**, 374 (1983); B. L. Gyorffy, D. D. Johnson, F. J. Pinski, D. M. Nicholson, and G. M. Stocks, in *Alloys Phase Stability,* Vol. 163 of *NATO Advanced Study Institute, Series E: Applied Sciences,* edited by G. M. Stocks and A. Gonis (Kluwer, Boston, 1989), pp. 421–468; J. B. Staunton, B. L. Györffy, D. D. Johnson, FJ. Pinski, and G. M. Stocks, *ibid.,* pp. 469–507.

[22] The Korringa-Kohn-Rostoker (KKR) electronic-structure method is, of course, properly analytic. The coherent-potential approximation (CPA) has been shown to be properly analytic, or Herglotz. See E. Muller-Hartmann, Solid State Commun. **12**, 1269 (1973), and F. Ducastelle, J. Phys. C **7**, 1795 (1974).

[23] D. D. Johnson, F. J. Pinski, and G. M. Stocks, Phys. Rev. B **30**, 5508 (1984); F. J. Pinski and G. M. Stocks, *ibid.* **32**, 4204 (1985).

[24] R. Zeller, J. Dentz, and P. A. Dederichs, Solid State Commun. **44**, 993 (1982); A. R. Williams, P. J. Feibelman, and N. D. Lang, Phys. Rev. B **26**, 5433 (1982).

[25] G. Reis and H. Winter, J. Phys. F **9**, 1589 (1979).

[26] G. M. Stocks, W. M. Temmerman, and B. L. Györffy, in *Electrons in Disordered Metals and at Metallic Surfaces,* Vol. 42 of *NATO Advanced Study Institute, Series B: Physics,* edited by P. Phariseau, B. L. Györffy, and L. Scheire (Plenum, New York, 1979), p. 193.

[27] F. J. Pinski, D. M. Nicholson, G. M. Stocks, W. H. Butler, D. D. Johnson, and B. L. Györffy, in *Proceedings of the Third International Conference on Supercomputing,* Boston, 1988, edited by L. P. Kartashev and S. I. Kartashev (International Supercomputing Institute, St. Petersburg, FL, 1988).

[28] L. Vegard, Z. Phys. **5**, 17 (1921); Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem. **67**, 239 (1928).

[29] G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook,* 2nd ed. (MIT Press, Cambridge, 1971). Also see W. B. Pearson, *A Handbook of Lattice Spacings and Structure of Metals and Alloys* (Pergamon, New York, 1964).

[30] R. Hultgren, P.D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelly, *Selected Values of the Thermodynamic Properties of*

Binary Alloys (American Society For Metals, Metals Park, Ohio, 1973), p. 818.

[31] M. Ahlers, in *Progress in Materials Science* (Pergamon, New York, 1987), Vol. 30, pp. 135–186.

[32] P. E. A. Turchi, G. M. Stocks, W. H. Butler, D. M. Nicholson, and A. Gonis, Phys. Rev. B **37**, 5982 (1988).

[33] P. L. Leath, J. Phys. C **6**, 1559 (1973).

[34] B. Drittler, M. Weinert, R. Zeller, and P. A. Dederichs, Phys. Rev. B **39**, 930 (1989).

[35] O. Kubaschewski, and J. A. Catterall, *Thermodynamic Data of Alloys* (Pergamon, New York, 1956).

[36] A. Messiah, *Quantum Mechanics,* edited by G. M. Temmer (North-Holland, Amsterdam, 1963), Vol. I, p. 404.