Density-Functional Theory for Random Alloys: Total Energy within the Coherent-Potential Approximation

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A density-functional–based theory is developed for calculation of the total energy and pressure of random substitutional alloys within the Korringa-Kohn-Rostoker coherent-potential approximation. The theory is used to calculate the concentration variation of the equilibrium lattice spacing of α-phase $\mathrm{Cu}_c\mathrm{Zn}_{1-c}$ alloys. We find, in agreement with experiment, that the variation is almost linear and that it deviates from Vegard's rule.

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In the modern world metallic alloys are used in an enormous variety of applications. The reasons for this ubiquitous use revolve around the possibility of modifying their properties—strength, ductility, corrosion resistance, thermal and electrical properties, etc.—to meet specific engineering requirements. Because most commercial alloys are complex multiphase mixtures, it is important that the phase relationships and the mechanisms responsible for phase stability be understood at the most basic level. At the microscopic level this means parameter-free theoretical models which treat, on an equal footing, all of the possible alloy phases that can occur: pure metals, possible ordered intermetallic compounds (stable and unstable), and possible disordered solid solutions.

During the last few years it has become clear that density-functional theory[1] (DFT) in the local-density approximation[2] (LDA) provides a sound, *ab initio*, theoretical basis for calculating the ground-state properties of pure metals[3] and ordered compounds.[4]. Consequently, DFT provides a logical starting point for a general theory of alloy phase stability provided it can be extended to the calculation of the total energy, etc., of the relevant disordered solid solutions.

In this Letter we present expressions for calculating the total energy and pressure of random substitutional alloys. They are based on DFT and the self-consistent Korringa-Kohn-Rostoker coherent-potential approximation[5] (KKR-CPA) method for calculation of the electronic structure of random alloys. Furthermore, we show results for the concentration dependence of the equilibrium lattice spacing of α-phase $\mathrm{Cu}_c\mathrm{Zn}_{1-c}$ random alloys using the new expressions.

The DFT rests on the theorem that the total energy $E[\rho(\mathbf{r})]$ is a unique functional of the electron density $\rho(\mathbf{r})$ and that the minimization of $E[\rho(\mathbf{r})]$ with respect to $\rho(\mathbf{r})$ leads to a set of single-particle-like equations, the self-consistent solution of which gives the ground-state charge density and energy. For ordered systems, solving of the DFT equations (in the local approximation) is straightforward because the effective electron-ion potential $V(\mathbf{r})$ is local, and the underlying translational symmetry allows the use of modern high-speed band-theory algorithms for solving the Schrödinger equation.[3]

The applicability of DFT is not, in principle, affected by the loss of translational symmetry in random alloys. However, two major obstacles render a direct solution intractable. First, the effective potential $V(r,\{\zeta_i\})$ is not periodic since it depends on the particular alloy configuration (specified by a set of site occupation variables ζ_i). Second, experiments measure configurationally averaged properties. The straightforward approach to the calculation of such averages would be to calculate the property for each member of an ensemble of alloy configurations and then to average with respect to the probability of occurrence $P(\{\zeta_i\})$ of that member of the ensemble. Thus the configurational average $\langle E\rangle$ of the total energy is $\langle E\rangle = \sum P(\{\zeta_i\})E(\{\zeta_i\})$ where the summation is over all possible configurations compatible with the concentrations of the alloying species. Obviously, an alternative path must be sought.

The modern *ab initio* theory of the electronic structure of random alloys is based on the KKR-CPA method.[5,6] The relative simplicity of the KKR-CPA method springs from the fact that it is a theory of the configurationally averaged properties themselves. The Hamiltonian, on which the method is based, is for a random array of nonoverlapping muffin-tin potentials $v_\alpha(\mathbf{r}-\mathbf{R}_i)$ centered on the lattice sites $\mathbf{R}_i$, there being as many different kinds of muffin-tin wells as there are atomic species α. The essence of the CPA is to replace the random array of real muffin-tin wells v_α by an ordered array of effective wells v_c. The scattering properties of v_c are then determined self-consistently, in a single-site mean-field sense, from the requirement that an electron traveling in an infinite array of v_c's undergoes, *on average*, no further scattering upon replacement of a single v_c potential with the v_α potentials. Once the scattering properties of a single v_c are known, such quantities as species-decomposed average densities of states $\bar{n}_\alpha(\epsilon)$ and charge densities $\bar{\rho}_\alpha(\mathbf{r})$ can be calculated straightforwardly.[7]

The self-consistent KKR-CPA method makes the partially averaged charge densities $\bar{\rho}_\alpha(\mathbf{r})$ consistent with the potential functions $v_\alpha(\mathbf{r})$.[8] In keeping with the single-site nature of the CPA, $v_\alpha(\mathbf{r}-\mathbf{R}_i)$ is regarded as being an appropriate single-site average potential and is obtained by associating with each site i the nuclear and electronic charge densities $Z\delta(\mathbf{r}-\mathbf{R}_i)$ and $\bar{\rho}_\alpha(\mathbf{r}-\mathbf{R}_i)$ and by averaging over the occupancy of all other sites $j\neq i$, i.e., associating with them the average nuclear and electronic charge densities

$$\bar{Z}\delta(\mathbf{r}-\mathbf{R}_j)=\sum\nolimits_\alpha c_\alpha Z_\alpha \delta(\mathbf{r}-\mathbf{R}_j)$$

and $\bar{\rho}(\mathbf{r}-\mathbf{R}_j)=\sum_\alpha c_\alpha \bar{\rho}_\alpha(\mathbf{r}-\mathbf{R}_j)$. In the interstitial volume Ω_0 the potential is fixed by taking the interstitial charge density $\bar{\rho}_0$ to be a constant $\bar{\rho}_0=\sum_\alpha c_\alpha \bar{\rho}_0^\alpha$ where

$$\bar{\rho}_0^\alpha \Omega_0 = Z^\alpha - \int_0^{r_{\mathrm{MT}}} dr\, 4\pi r^2 \bar{\rho}_\alpha(\mathbf{r}),$$

r_{MT} being the radius of the muffin-tin sphere. Setting the interstitial potential to be the zero of energy then[8] gives

$$v_\alpha(\mathbf{r}) = -\frac{2Z^\alpha}{r} + 8\pi\left[\int_0^r dr_1\, r_1^2\left(\frac{1}{r}-\frac{1}{r_1}\right)\bar{\rho}_\alpha(r_1) + \int_0^{r_{\mathrm{MT}}} dr_1\, r_1 \bar{\rho}_\alpha(r_1)\right] + \mu_{\mathrm{xc}}(r;\bar{\rho}_\alpha) - \mu_{\mathrm{xc}}(\bar{\rho}_0) + \left(\frac{C}{a}\right)\bar{\rho}_0\Omega_0, \qquad (1)$$

where C is a constant that depends on the crystal structure,[3] a is the lattice spacing, and μ_{xc} is the LDA exchange-correlation potential.[9]

The above self-consistent KKR-CPA method has been applied to a number of alloy systems with considerable success.[10] These results, taken together with the results of earlier, non-self-consistent calculations,[5] lead to the conclusion that the method may be of sufficient accuracy to allow for the calculation of total energies, etc. However, the difficulty with the method is that the self-consistency step (and, therefore, the variational step in DFT) and the configurational averaging step are inextricably mixed together. Consequently, it has not yet been possible to begin with the DFT equations for the configurational average of the total energy and to derive a set of self-consistency equations that in a self-consistent single-site approximation would require the calculation of single-site charge densities, etc., using the KKR-CPA. Given this situation, in the following we take a different tack. We begin from the self-consistent formulation of the KKR-CPA and show that an expression for the total energy can be derived that is consistent with the KKR-CPA and that the energy expression satisfies many of the conditions usually associated with DFT, e.g., stationarity.

We begin with Maxwell's relation $N(\mu) = -(\partial\Omega/\partial\mu)_{T,V}$ between the grand potential Ω of the electron system, the number of particles $N(\mu)$, and the chemical potential μ. By recalling that

$$N(\mu)=\int_{-\infty}^{\infty} d\epsilon\, n(\epsilon) f(\epsilon-\mu)$$

where $f(\epsilon-\mu)$ is the Fermi function and $n(\epsilon)$ is the density of states, we may integrate with respect to μ. Taking the zero-temperature limit and averaging over all configurations, we obtain the starting expression for the configurationally averaged ground-state energy[11]:

$$E(V,\mu)-\mu\bar{N}(\mu) = \sum_{i\neq j}\frac{\bar{Z}^2}{|\bar{\mathbf{R}}_i-\bar{\mathbf{R}}_j|} - \int_{-\infty}^{\infty} d\epsilon\, \bar{N}(\epsilon;\mu)\theta(\mu-\epsilon) + \int_{-\infty}^{\mu} d\mu' \int_{-\infty}^{\infty} d\epsilon\, \frac{\partial \bar{N}(\epsilon;\mu')}{\partial\mu'}\theta(\mu'-\epsilon), \qquad (2)$$

where $\bar{N}(\epsilon;\mu)$ denotes the configurationally averaged integrated density of states per site. For orientation we note that the first term in Eq. (2) is the sum of the single-particle eigenvalues, and the second is the double-counting correction.

Within the KKR-CPA, $\bar{N}(\epsilon;\mu)$ is given by[12]

$$\bar{N}(\epsilon;\mu) = N_0(\epsilon) - \pi^{-1}\,\mathrm{Im}[\ln\|\underline{t}_c^{-1}-\underline{g}\| + \sum\nolimits_\alpha c_\alpha \ln\|\underline{1}+(\underline{t}_\alpha^{-1}-\underline{t}_c^{-1})\underline{\tau}^c\|], \qquad (3)$$

where $\underline{t}_\alpha$ and $\underline{t}_c$ are t matrices corresponding to v_α and v_c, $\underline{g}$ is the matrix of real-space structure constants, and $\underline{\tau}_c$ is the diagonal part of the total scattering operator for an ordered lattice of v_c's. The underscore denotes matrices in both the angular momentum variable $L = (l,m)$ and the site index n, and $||\phi||$ denotes the determinant. By use of Eq. (3), Eq. (2) may be recast as

$$\bar{E} = \sum_{i\neq j} \frac{\bar{Z}^2}{|\bar{\mathbf{R}}_i - \bar{\mathbf{R}}_j|} \int_{-\infty}^{\infty} d\epsilon\, \epsilon \sum_\alpha c_\alpha \bar{n}_\alpha(\epsilon)\theta(\mu-\epsilon) - \int_\Omega d^3r \int_{-\infty}^{\infty} d\mu' \sum_\alpha c_\alpha \bar{\rho}_\alpha(\mathbf{r}) \frac{\partial v_\alpha(\mathbf{r})}{\partial \mu'} \theta(\mu - \mu'). \tag{4}$$

If we take for $v_\alpha(\mathbf{r})$ the muffin-tin potential Eq. (1), $\bar{E}$ can be written in the form

$$\bar{E} = \sum\nolimits_\alpha c_\alpha E^{\mathrm{J}}(\bar{\rho}_\alpha, \bar{\rho}_0), \tag{5}$$

where E^{J} is an expression of the same form as that obtained by Janak [see Eq. (25) of Ref. 13] except that the pure metal muffin-tin and interstitial charge densities $\rho(\mathbf{r})$ and ρ_0 are replaced by $\bar{\rho}_\alpha(\mathbf{r})$ and $\bar{\rho}_0$.

Equation (5) is an appealing result for several reasons. First, once a self-consistent KKR-CPA calculation has been performed, an accurate evaluation of the total energy is straightforward and all of the subtle single-particle/double-counting cancellations effected in Janak's[13] original formulation apply. Second, in the pure-metal limits, Eq. (5) reduces to Janak's expression. Third, the simple form of the total-energy expression is due primarily to the fact that, within the CPA, $\bar{N}(\epsilon)$ is stationary with respect to variations in t_c,[14] and thus the mean-field potential reconstruction method embodied in Eq. (1) and the mean-field CPA condition for determining t_c, etc., have meshed together to produce a simple result. However, it should be noted that the particular choice of the interstitial charge density is also of importance in obtaining certain cancellations leading to Eq. (5). Fourth, Eq. (5) appeals to the intuition and can, in fact, be obtained by consideration of a particular average of the Coulomb energy of the component charge density. The procedure is similar to that described above in connection with selection of the muffin-tin potentials. Such an approach, however, obscures the connection to Maxwell's relation and the role played by the CPA in the maintaining of internal consistency. Finally, the current formulation has a number of important properties in common with standard DFT. It can be shown that $\bar{E}$ is stationary with respect to independent variations in the component charge densities, i.e., $\delta\bar{E}[\bar{\rho}_A, \bar{\rho}_B, \ldots]/\delta\bar{\rho}_\alpha(\mathbf{r}) = 0$, and that the functional derivative of the potential energy with respect to $\bar{\rho}_\alpha(\mathbf{r})$ returns the potential $v_\alpha(\mathbf{r})$.

In a similar manner we may also obtain an expression for the configurationally averaged pressure P within the KKR-CPA formalism. The result is

$$\bar{P} = \sum\nolimits_\alpha c_\alpha P^{\mathrm{J}}[\bar{\rho}_\alpha, \bar{\rho}_0] \tag{6}$$

where, once again, P^{J} is the expression of Janak [see Eq. (24) of Ref. 13]. We note that the partial pressures P_α may be obtained as $P_\alpha = P_\alpha^{\mathrm{J}}$ + (surface terms) and that upon concentration averaging, the surface terms cancel. They vanish for a pure metal by Gauss's theorem.

In order to test the above formalism we have applied it to the study of the concentration variation of the equilibrium lattice spacing of the Hume-Rothery alloys $\mathrm{Cu}_c\mathrm{Zn}_{1-c}$. In these calculations we used the exchange-correlation potential of Hedin and Lundqvist.[9]

In Fig. 1 we show the calculated equilibrium lattice spacing of α-phase $\mathrm{Cu}_c\mathrm{Zn}_{1-c}$ alloys having $c = 1.0$, 0.9, 0.8, and 0.7. The equilibrium was located by finding that lattice spacing for which the pressure is zero. Also shown in Fig. 1 are the measured room-temperature values[15] as well as calculated values for $\mathrm{Cu}_{0.5}\mathrm{Zn}_{0.5}$ and pure zinc for an fcc lattice.

Over the concentration range of the α phase ($c \gtrsim 0.7$) we obtain an almost linear concentration variation of the lattice spacing. For higher zinc concentration we find a small departure from linearity. In the α phase the initial slope is 0.0045 a.u./at.%; at room temperature the experimental value is 0.0042 a.u./at.%. Taking the experimental value for zinc in the hcp phase and converting that to an equivalent fcc lattice spacing gives 7.352 a.u. Vegard's rule[16] of assuming the lattice spacing to interpolate linearly between the pure metals gives a slope of 0.0054 a.u./at.%. The negative departure from Vegard's rule seen in the α phase is well reproduced by the theory.

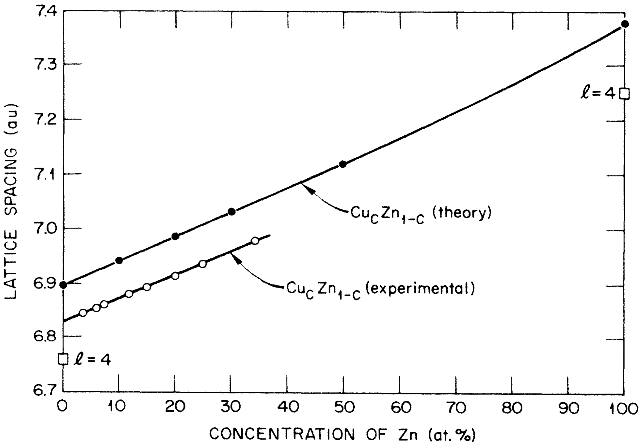

FIG. 1. Concentration variation of the lattice spacing of α-phase $\mathrm{Cu}_c\mathrm{Zn}_{1-c}$ alloys. Calculated: solid circles. Experimental: open circles.

Use of the room-temperature lattice spacings in Fig. 1 makes the agreement between theory and experiment appear better than it is. With use of the calculated and measured values[3] of 6.895 and 6.809 a.u. for copper at $T=0$ K (cf. 6.832 a.u. at 300 K) the error is 1.3%. The major part of this discrepancy is due to the truncation of the angular momentum summations in our calculations at $l=2$. For copper, inclusion of $l=3$ and 4 terms gives an equilibrium lattice spacing of 6.767 a.u.,[3] which is within 0.6% of experiment. Presumably, inclusion of these terms in the KKR-CPA will result in a similar residual error. The absolute error notwithstanding, we view the agreement between theory and experiment pleasing, this being the first *ab initio* calculation of the lattice spacing of a random alloy.

Preliminary calculations of the heats of mixing $\Delta E = \bar{E} - cE^{\mathrm{Cu}} - (1-c)E^{\mathrm{Zn}}$ where E^{Cu} (E^{Zn}) is the ground-state energy of Cu (Zn) are also encouraging. They are negative and of the correct order of magnitude. For example, near the limit of room-temperature solubility ($c=0.3$), $\Delta E = -3.8$ mRy, which is roughly one-half the experimental value. However, without the inclusion of the higher angular momentum components, we do not regard them to have fully converged. We are currently including these additional contributions and will give a full report of the results elsewhere.

In this Letter we have extended DFT to treat the energetics of random substitutional alloys within the KKR-CPA. The theory of the ground-state properties of random alloys is now on a sound footing, comparable to that for pure metals and ordered alloys. Consequently, it should be possible to contemplate *ab initio* studies of alloy formation, of alloy phase stability, and of the forces which drive ordering processes in alloys. The theory is applicable to alloys containing any number of components, and is straightforward to generalize to multi-sublattice crystal structures, or to treatment of alloys that are magnetic by means of the local spin-density approximation.[17] Since the theory is a mean-field theory of the electronic structure and is easily extended to finite temperature, it also fits logically into a mean-field theory of the statistical mechanics of alloy configurations.[18]

The strength of this formulation is the internal consistency of its components, i.e., Maxwell's relation, the CPA, the muffin-tin potential, the total energy, and the pressure. The results here are particular to the CPA and the muffin-tin Hamiltonian. It may be possible to apply these methods to alternative Hamiltonians or averaging schemes, e.g., tight-binding CPA; however, great care should be taken to insure that the consistency of the theory is maintained.

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