VOLUME 87, NUMBER 15 PHYSICAL REVIEW LETTERS 8 OCTOBER 2001

# Anisotropic Lattice Distortions in Random Alloys from First-Principles Theory

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(Received 12 February 2001; published 19 September 2001)

Within the framework of the exact muffin-tin orbitals (EMTO) theory we have developed a new method to calculate the total energy for random substitutional alloys. The problem of disorder is treated within the coherent potential approximation (CPA), and the total energy is obtained using the full charge density (FCD) technique. The FCD-EMTO-CPA method is suitable for determination of energy changes due to anisotropic lattice distortions in random alloys. In particular, we calculate the elastic constants of the Cu-rich face centered cubic Cu-Zn alloys ($\alpha$-brass) and optimize the $c/a$ ratio for the hexagonal Zn-rich alloys for both the $\epsilon$ and $\eta$ phases.

DOI: 10.1103/PhysRevLett.87.156401 PACS numbers: 71.15.Nc, 71.15.Ap, 71.20.Be

The calculation of the total energy of a solid is one of the most important problems of electronic theory, and density functional theory [1] provides one with a theoretical foundation for solving this problem. However, the most efficient computational scheme for the solution of the one electron equations depends on the system at hand, as well as on the required level of accuracy. For example, the spherical approximation for the one electron density and potential used in such popular techniques for electronic structure calculations as the Korringa-Kohn-Rostoker (KKR) or the linear muffin-tin orbital (LMTO) methods is often sufficient for the characterization of properties of close packed crystals on a rigid or uniformly distorted (e.g., compressed or expanded as a whole) lattice. However, it fails to reproduce the behavior of the total energy upon anisotropic lattice distortions. In order to calculate, for example, elastic properties of a random alloy, where the accuracy of the conventional KKR or LMTO methods are known to be insufficient, more advanced full-potential technique is needed. Therefore, one has to rely on very crude approximations within alloy theory, like the virtual crystal approximation [2]. Alternatively, one has to carry out extremely time-consuming calculations for big supercells, or to be restricted to few selected concentrations on the face centered or body centered cubic underlying lattices for which the so-called special quasirandom structures have been constructed [3].

On the other hand, a very successful approximation which allows one to perform calculations for systems with substitutional disorder is the coherent potential approximation (CPA). It was introduced by Soven [4], and Györffy [5] has formulated the CPA in the framework of the multiple scattering theory. Nowadays it has become a state-of-the-art technique for electronic structure calculations. It has been shown that within CPA one can calculate accurate total energies and ground state properties (lattice parameters, bulk moduli, mixing enthalpies, etc.) of many alloy systems [6,7]. However, currently the CPA is mostly used in the framework of the KKR or LMTO methods; therefore its application is restricted to close packed systems, and, with few exceptions [8], the only type of distortion one can allow for in these calculations is a uniform change of the volume.

In this Letter we present a formulation of the coherent potential approximation within the basis set of the so-called *exact muffin-tin orbitals* (EMTO) that has recently been developed by Andersen and co-workers [9], and show that this method, combined with the *full charge density* (FCD) formalism [10,11], allows one to calculate the energy differences of a random alloy with an accuracy, which is sufficient to treat the effect of anisotropic lattice distortions. We demonstrate the application of the FCD-EMTO-CPA method in the description of the structural and elastic properties of $\mathrm{Cu}_{1-x}\mathrm{Zn}_x$ random alloy, which is a classical system for testing new alloy theories [6,12,13]. Here, for the first time, we investigate two questions: (a) the calculation of the tetragonal shear moduli for $\alpha$ brass ($x \lesssim 0.38$), which has the face centered cubic (fcc) structure, and (b) the optimization of the $c/a$ ratio for hexagonal (hcp) $\epsilon$ brass ($0.78 \lesssim x \lesssim 0.86$) and $\eta$ brass ($x \gtrsim 0.97$) [14]. We show that there is a clear distinction between the two hexagonal phases in the Cu-Zn system, seen as two local minima of the total energy as a function of volume and $c/a$ that appears for certain alloy concentrations.

In the EMTO theory [9] the one electron effective potential is represented by the optimized overlapping muffin-tin potential [9,10,15], which is the best possible spherical approximation to the full one electron potential. The one electron wave functions are expanded in terms of the EMTO's ($Z_{RL}$), which are defined for each lattice site $\mathbf{R}$ and for each angular momentum quantum number $L \equiv (l, m)$ with $l \leq l_{\max}$ (usually $l_{\max} = 3$). The EMTO's are constructed from the *screened spherical waves,* which are solutions of the wave equation with boundary conditions given in conjunction with nonoverlapping hard spheres [9] with radii $a_R$. Inside the overlapping potential spheres the low $l$ ($l \leq l_{\max}$) projections of $Z_{RL}$ onto the spherical harmonics $Y_L(\hat{r})$ are the *partial waves,* i.e., the regular solutions of the radial Schrödinger equation. The matching between the screened spherical waves and the *partial waves* is realized by additional free-electron solutions [9].

In order to calculate the total energy of a random alloy within the CPA one has to know the average alloy density of states $\langle N \rangle$ and the average electron density $n^i$ for each alloy component $i$ [6]. The former is determined from the average Green function

$$\langle G(z) \rangle \equiv \int_{BZ} \sum_{R'L'RL} \tilde{g}_{R'L'RL}(z,\mathbf{k}) \dot{S}_{RLR'L'}(z,\mathbf{k})\, d\mathbf{k} - \sum_i c^i \sum_{RL} \left[ g^i_{RLL}(z) \dot{D}^i_{Rl}(z) + \left( \frac{\dot{D}^i_{Rl}(z)}{D^i_{Rl}(z)} - \frac{1}{z - e^i_{Rl}} \right) \right]. \tag{1}$$

Here the overdot stands for the energy derivative and $l, l' \leq l_{\max}$. The coherent Green function, $\tilde{g}$, and the slope matrix [9], $S$, depend on the Bloch vector $\mathbf{k}$ from the first Brillouin zone. $z$ denotes the complex energy and $e^i$ are the real zeros of the logarithmic derivative function, $D^i$, corresponding to the potential of the alloy component of concentration $c^i$. The coherent Green function and Green functions for alloy components, $g^i$, are determined from the self-consistent solution of the CPA equations

$$\sum_{R''L''} a_{R'} [S_{R'L'R''L''}(z,\mathbf{k}) - \tilde{D}_{R'L'R''L''}(z)] \tilde{g}_{R''L''RL}(z,\mathbf{k}) = \delta_{R'R} \delta_{L'L},$$

$$g^i_{RLL'}(z) = \tilde{g}_{RLRL'}(z) + \sum_{L''L'''} \tilde{g}_{RLRL''}(z) [D^i_{Rl''}(z) \delta_{L''L'''} - \tilde{D}_{RL''RL'''}(z)] g^i_{RL'''L'}(z)$$

$$\tilde{g}_{RLRL'}(z) = \sum_i c^i g^i_{RLL'}(z),$$

where $l, l', l'' \leq l_{\max}$, and $\tilde{D}$ is the coherent logarithmic derivative function.

The main difference of the EMTO expression (1) from the similar expressions for the atomic sphere approximation (ASA) based CPA Green functions, e.g., ASA-KKR-CPA or ASA-LMTO-CPA Green functions, is the first term on the right hand side of (1) that assures a proper normalization of the one electron states [9]. Therefore, within the single site approximation the Green function (1) leads to the exact density of states for the optimized overlapping muffin-tin potential.

In the framework of the EMTO-CPA formalism, the average electron density for each alloy component is represented in one center form around site $\mathbf{R}$, i.e., $n^i(\mathbf{r}) = \sum_R n^i_R(\mathbf{r}_R) \equiv \sum_{RL} n^i_{RL}(r_R) Y_L(\hat{r}_R)$. Inside the Wigner-Seitz cell the partial components $n^i_{RL}(r_R)$ are expressed in terms of the density matrix

$$\mathcal{D}^i_{RL'L}(z) \equiv \begin{cases} g^i_{RL'L}(z) + \frac{\delta_{L'L}}{a_R \dot{D}^i_{Rl}(z)} \left( \frac{\dot{D}^i_{Rl}(z)}{D^i_{Rl}(z)} - \frac{1}{z - e^i_{Rl}} \right) & \text{if } l, l' \leq l_{\max}, \\ \sum_{R''L''} \int_{BZ} \tilde{g}_{RL'R''L''}(z,\mathbf{k}) S_{R''L''RL}(z,\mathbf{k})\, d\mathbf{k} & \text{if } l' \leq l_{\max} \quad \text{and} \quad l > l_{\max}, \\ \sum_{R''L''R'''L'''} \int_{BZ} S_{RL'R''L''}(z,\mathbf{k}) \tilde{g}_{R''L''R'''L'''}(z,\mathbf{k}) S_{R'''L'''RL}(z,\mathbf{k})\, d\mathbf{k} & \text{if } l', l > l_{\max}, \end{cases}$$

as

$$n^i_{RL}(r_R) = \frac{1}{2\pi i} \oint \sum_{L''L'} C^L_{L''L'} Z^i_{Rl''}(z, r_R) \times \mathcal{D}^i_{RL''L'}(z) Z^i_{Rl'}(z, r_R)\, dz, \tag{2}$$

where $C^L_{L''L'}$ are the real harmonic Gaunt coefficients, and the energy integral includes the occupied states. Because of the one center form of the charge density, in Eq. (2) the $l''$ and $l'$ summations include the *higher* terms as well, which, in practice, are truncated at $l^h_{\max} = 8$–$12$ [10]. This allows one to calculate the full charge density with an accuracy higher than for conventional KKR calculations, where only terms with $l \leq l_{\max}$ are included.

The overlapping muffin-tin potential for each alloy component, $v^i_{mt}(\mathbf{r})$, is constructed from the average electron density $n^i$ within the *spherical cell approximation* (SCA). Details about the solution of the Poisson equation within the SCA are given in Refs. [10,15]. The effect of the charge transfer on the electrostatic potential is taken into account using the *screened impurity model* (SIM) [16]. Finally, the total energy of the random alloy is calculated as

$$E_{\text{tot}} = \frac{1}{2\pi i} \oint z \langle G(z) \rangle\, dz - \sum_R \sum_i c^i \int_{\Omega_R} v^i_{mt}(\mathbf{r}) n^i(\mathbf{r})\, d\mathbf{r} + F_{\text{inter}}[n^i] + \sum_R \sum_i c^i (F^i_{\text{intra}R}[n^i_R] + E^i_{\text{xc}R}[n^i_R]) - \sum_i c^i \frac{\alpha_c}{w} \left( Q^i_R - \sum_i c^i Q^i_R \right)^2, \tag{3}$$

where $F_{\text{inter}}$ is the average Madelung energy, and $F^i_{\text{intra}R}$ and $E^i_{\text{xc}R}$ are the electrostatic and exchange-correlation energies due to the charges from the Wigner-Seitz cell at $\mathbf{R}$, $\Omega_R$. The last term in (3) is the SIM correction to the electrostatic energy [16], $\alpha_c \approx 0.6$, $w$ is the average atomic radius, and $Q^i_R$ denotes the total number of electrons inside the cell for the alloy component $i$. The individual energy functionals are evaluated using the full charge density technique [11].

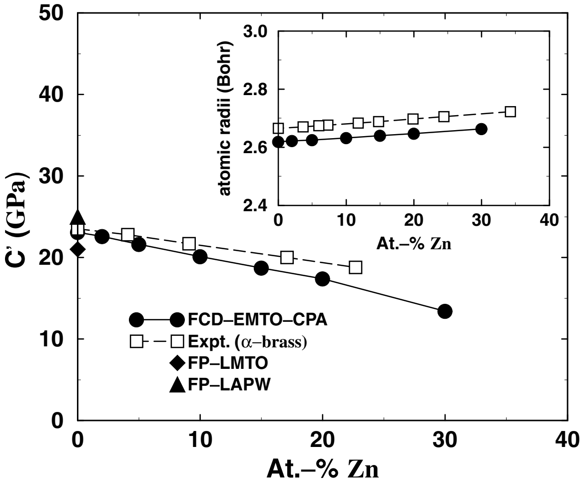

FIG. 1. Comparison between the theoretical (FCD-EMTO-CPA: present calculation; FP-LMTO: Ref. [2]; FP-LAPW: Ref. [20]) and experimental [19] tetragonal elastic constant and equilibrium atomic radius (shown in the inset) for $\alpha$ brass as a function of the concentration of zinc.

In Fig. 1 we present our theoretical results [17,18] for the tetragonal elastic constant ($C'$) and equilibrium atomic radius (shown in the inset), and compare them to the available experimental data [19]. For pure Cu results of full-potential calculations [2,20] are also shown, and they agree well with our result. In the $\alpha$ phase an increase of the Zn concentration leads to a decrease of $C'$ and an increasing equilibrium volume. The average softening of $C'$ below 30 at. % Zn is $-0.30$ GPa per at. % Zn compared to the measured value of $-0.23$ GPa per at. % Zn [19]. We have found that this trend correlates well with the fcc-bcc structural energy difference, in accordance with the previous observations obtained within the virtual crystal approximation for the $4d$ and $5d$ transition metal alloys [2]. The $E_{\text{tot}}^{\text{bcc}} - E_{\text{tot}}^{\text{fcc}}$ energy difference for $\alpha$ brass, calculated using the FCD-EMTO-CPA method, decreases nearly linearly with $x$ from 1.5 mRy at $x = 0$ and it becomes zero at $x \approx 0.4$.

The theoretical $c/a$ axial ratios for the hcp Cu-Zn structures [17,21] and the corresponding equilibrium atomic radii along with the available experimental data [14] are plotted in Fig. 2. For pure Zn our result is also compared with those obtained by means of full potential calculations in different studies [22,23]. It is well known that the calculated axial ratio in Zn depends to a large degree on the details of the calculations; in particular, it depends on the exchange-correlation functional, but it also depends on whether the calculations are done at the theoretical or experimental equilibrium volume. Furthermore, as it is visualized in the case of the $\text{Cu}_{0.07}\text{Zn}_{0.93}$ alloy in Fig. 3, the energy minimum is very shallow around the equilibrium. Thus, the agreement between the full potential and the present FCD-EMTO results for pure Zn is satisfactory.

The anomalously large axial ratio of pure Zn is calculated to be reduced by 2.4% at 3 at. % Cu, in very good agreement with the experimental result. At low Cu concentrations we have found that the $\eta$ phase, with large $c/a$ ratio, is the ground state structure of the copper-zinc alloy. With increasing Cu concentration a second total energy minimum in the volume versus axial ratio plane starts

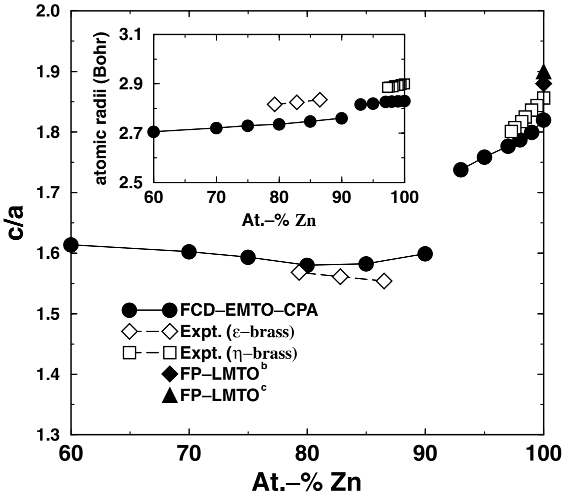

FIG. 2. Comparison between the theoretical (FCD-EMTO-CPA: present calculation; FP-LMTO$^{a}$: Ref. [22]; FP-LMTO$^{b}$: Ref. [23]) and experimental [14] hexagonal axial ratios and equilibrium atomic radii (shown in the inset) for $\epsilon$ and $\eta$ brass as functions of the concentration of zinc.

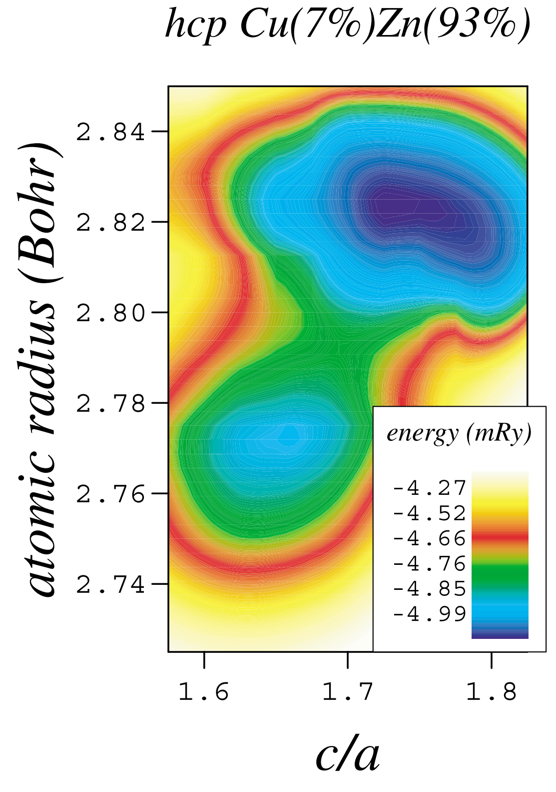

FIG. 3 (color). Total energy for the $\text{Cu}_{0.07}\text{Zn}_{0.93}$ random alloy calculated by the FCD-EMTO-CPA method as a function of the average atomic radius and hexagonal axial ratio, $c/a$.

to develop. This situation is demonstrated in Fig. 3, where the two minima correspond to 1.74 and 1.64 axial ratios, and to 2.82 and 2.77 bohr atomic radii, respectively. Thus, though $\eta$ and $\epsilon$ brass in the Cu-Zn system have the same hexagonal crystal structure, they indeed represent two different phases, each having its own (local) energy minimum. For $x \lesssim 0.9$ the second energy minimum becomes stable relative to the first one, and the system stabilizes in the $\epsilon$ phase with a hcp structure and $c/a \lesssim 1.6$. The axial ratio in the $\epsilon$ phase initially decreases with the Cu concentration, and above 20 at. % Cu it shows an increase towards the ideal value of 1.63. In both of the $\eta$ and $\epsilon$ phases the equilibrium volume changes continuously with the concentration, but both theory and experiment exhibit a small discontinuity around $x = 0.9$, corresponding to the $\eta$ to $\epsilon$ isostructural phase transition.

In summary, we have developed an *ab initio* technique for the electronic structure calculations, which allows one to determine the total energy differences with the same accuracy as for the full-potential methods, but, in contrast to the latter, it can be used for random substitutional alloys. We note that the ability of the presented technique to describe correctly the anisotropic lattice distortions makes it potentially very attractive for combining it with more powerful methods within the alloy theory which go beyond the single site approximation, like the locally self-consistent Green function method [13]. In this case one will be able to treat alloys with short-range order and with local lattice relaxations [13,24].

The Swedish Research Council, Natural and Engineering Sciences, the Swedish Foundation for Strategic Research, and Royal Swedish Academy of Sciences are acknowledged for financial support.

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