

First-Principles Study of Phase Stability in Cu-Zn Substitutional Alloys

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A parameter-free approach to phase stability in Cu-Zn substitutional alloys is shown to describe order-disorder phenomena and structural transformations with remarkable accuracy. The method is based on a multiple-scattering description of the electronic structure properties of the random alloy. Configurational order is treated within the generalized perturbation method and the concentration-functional theory. Thermodynamical properties of α and β brasses are derived from the cluster variation method. This advanced scheme is of general validity and is expected to yield similarly accurate results for other Hume-Rothery alloys.

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The Cu-Zn alloy system has long been recognized as the prototypical representative of a class of alloys known as Hume-Rothery alloys [1,2]. For this class of materials, it is stated that phase stability properties are driven by the average number of valence electrons, or electron to atom ratio (e/a). This rule makes them called "electron phases," in contrast to alloys for which geometrical factors, or size ratio effects, govern phase stability. The purpose of this Letter is to clearly demonstrate the predictive power of a recently devised combination of quantum mechanics and statistical thermodynamics for describing equilibrium properties of Cu-Zn alloys exhibiting both fcc (α) and bcc (β) solid solutions as well as ordered compounds. This first-principles approach points, at least for the low-temperature behavior, to the importance of configuration-dependent properties, which evolve as a function of concentration, i.e., (e/a) ratio, therefore confirming one of the aforementioned Hume-Rothery rules. This study shows that a competition takes place between α - and β -based partially ordered alloys, at low temperature and in a narrow range of concentration, where a martensitic transformation occurs [3]. Our approach also reveals the ability of α -brass, around Cu_3Zn , to form long-period superstructures, at low temperature, as suggested by an estimate of antiphase boundary energy, and also by calculated and experimentally determined short-range-order diffuse scattering intensity [4]. Finally, it is shown that the vibrational contribution to the free energy, as expected, cannot be ignored for a proper description of phase stability properties at high temperature.

A clear distinction has to be made between Cu-rich and Zn-rich alloys. Indeed, the left part of the Cu-Zn phase diagram essentially deals with binary Cu-Zn alloys, as opposed to the Zn-rich part where complex phases (γ, δ, ϵ) based on a distorted bcc lattice indicate that their formation is vacancy (\square) induced. Hence, in principle,

one should consider a true ternary Cu-Zn- \square and the accompanied relaxation effects in order to describe this part of the phase diagram. This situation is reminiscent of what happens for other Hume-Rothery alloys, such as Cu-Al and Cu-Ge. In this study, we concentrate on the binary Cu-Zn system and no attempt is made to describe liquid alloys.

The quest for devising first-principles schemes to study alloy phase stability from a proper combination of quantum mechanics and statistical thermodynamics has been recently motivated by three factors. First, *ab initio* calculations of total energies within the local-density approximation are successful in predicting ground-state properties of substitutional alloys [5]. Second, the cluster variation method (CVM) or Monte Carlo simulations, used in conjunction with a three-dimensional Ising model, can accurately describe alloy phase stability properties at $T \neq 0$ K [6]. Finally, the link between these two fields was made possible by introducing approaches justifying an Ising-like expression for the ordering contribution to the total energy. Among them, one can mention the concentration-functional theory (CFT) and the generalized perturbation method (GPM) [6]. These approaches share the fundamental idea that any configurational state of order can be described from the unique knowledge of a random medium, or configurationally disordered state of matter, at any concentration. In this paper, for reasons discussed elsewhere [6,7], we apply the GPM approach to the self-consistent-field Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA) description of the chemically random medium [8,9]. Hence the total energy of any configuration of an alloy $A_{1-c}B_c$, at $T=0$ K, is given by two terms. The first one is the total energy of the random state, E_{CPA} , more conveniently expressed by the so-called mixing energy, $E_{\text{mix}}(c) = E_{\text{CPA}}(c) - (1-c)E_A - cE_B$, where $E_{A(B)}$ designates the total energy of pure species A (B). The second term, called the

ordering energy, takes, to lowest order in perturbation in the GPM framework, the following form:

$$\Delta E_{\text{ord}}(\{q_s\}) \approx \sum_s q_s V_s \text{ with } q_s = \frac{1}{2} c(n_s^{BB} - cn_s),$$

where n_s^{BB} and n_s refer to the number of BB pairs and total number of pairs, per site, associated with the s th-neighbor shell. V_s is an s th-neighbor effective pair interaction (EPI) given by $V_s = V_s^{AA} + V_s^{BB} - 2V_s^{AB}$. Any state of order is specified by a set of parameters $\{q_s\}$ which only depend on site occupancies. As uniquely justified from electronic-structure formalism, this ordering energy is driven by a Hamiltonian of the Ising-type with the concentration-dependent EPI insuring a rapid convergence of the above expansion [6-8]. In this approach, for most of the alloy cases studied thus far, the calculated multisite interactions are negligible.

The calculations of the total energies and EPIs for both α - and β -based Cu-Zn, as a function of concentration and lattice parameter, were performed on the basis of charge self-consistent CPA muffin-tin potentials up to an angular momentum index l equal to 3 and 2, respectively. The results are summarized in Fig. 1. Because of the extreme accuracy required to compute the details of phase stability properties, at $T \neq 0$ K, the relative structural stability energies between the α and β modifications of both pure Cu and pure Zn were obtained with the full-potential linearized augmented plane-wave method (FLAPW) in

which no shape approximation is imposed to the potential [10]. With reference to the α structure, the excess energies of +3 and +4 mRy/atom for Cu and Zn, respectively, compare well with recently calculated [11] and assessed values [12]. The mixing-energy curves, for both α - and β -based alloys, indicate a strong tendency toward phase formation which is confirmed by the predominantly positive sign of the EPIs in the entire range of concentration. Quantitatively, the EPIs of α -based alloys around Cu_3Zn compare well with the ones deduced from neutron diffuse scattering experiments [4]. Besides the concentration dependence of the EPIs, especially for β -based alloys around 40 at.% Zn, the first EPI [including the second-nearest-neighbor (nn) EPI of β] are at least an order of magnitude larger than the more distant ones [9]. EPIs beyond fourth and fifth nn shells for α - and β -based alloys, respectively, as well as multisite interactions are less than 0.1 mRy/atom. Hence, it is expected that these rapidly converged sets of EPIs will provide an accurate determination of the configurational energies. These EPIs, with the results of the ground-state properties of the Ising model for the fcc lattice, up to the fourth nn shell [13], indicate that LI_2 (or α') and LI_0 , for Cu_3Zn (CuZn_3) and CuZn , respectively, are the most probable ground states. Similarly, together with the results obtained for the Ising model applied to the bcc lattice up to the fifth nn shell (excluding V_4) [14], the sets of EPIs give DO_3 and $B2$ (or β') for Cu_3Zn (CuZn_3) and CuZn , respectively, as ground states.

At $T \neq 0$ K, the statistical thermodynamics was treated within the tetrahedron-octahedron (irregular tetrahedron) approximation of the CVM for fcc- (bcc-) based alloys with the energetic quantities displayed in Fig. 1. With only the equilibrium configurational contributions to the free energy computed with the CVM, for both lattices and the disordered as well as the ordered configurations mentioned previously, the phase diagram shown in Fig. 2(a) is obtained. In order to evaluate the effect of vibrational properties, we considered assessed values of the Debye temperature Θ_D for the pure species [15] and a linear interpolation of Θ_D for the alloy case. The vibrational contributions to the total free energy were calculated within the Debye theory, where configurational dependence was ignored. The resulting phase diagram, represented in Fig. 2(b), is now in striking agreement with its experimental counterpart, at least for the Cu-rich part. It shows that the typical curvature of the two-phase region ($\alpha + \beta$) is essentially explained by the leading effect of the excess vibrational entropy which characterizes β -based systems [16]. However, the low-temperature part of the incoherent phase diagram is unaffected by vibrational effects, and the following comments will be essentially valid for both diagrams of Fig. 2.

First, the critical order-disorder temperature for the β' to β transition, of the order of 740 K, compares very well with the experimental estimate of 730 K. Moreover, the β' phase is characterized by an ordering energy of about

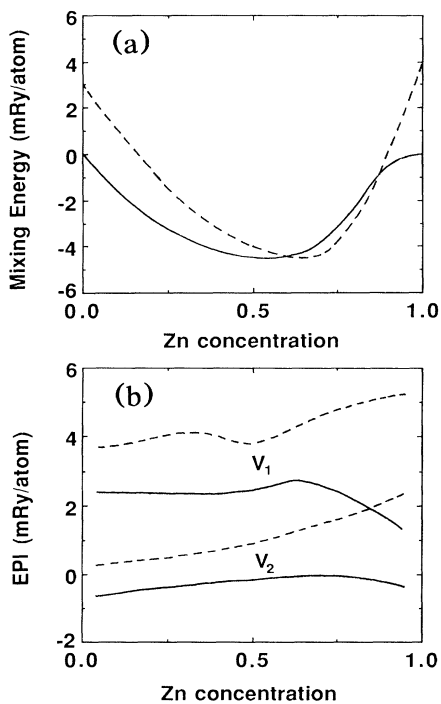


FIG. 1. (a) Mixing energies (fcc-based Cu and Zn are taken as references) and (b) EPI, in mRy/atom, as a function of Zn concentration, for fcc- (solid curve) and bcc- (dashed curve) based Cu-Zn alloys.

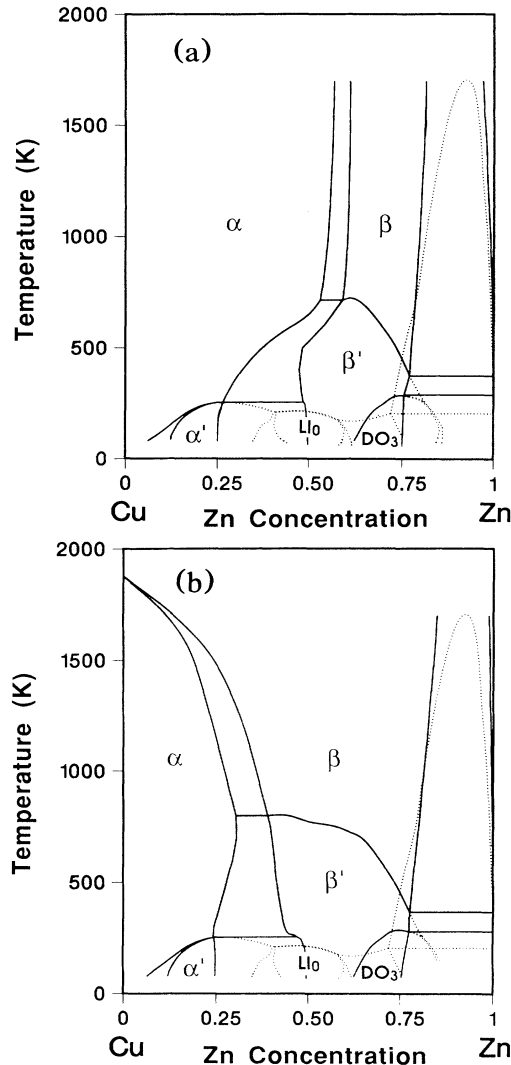


FIG. 2. Calculated Cu-Zn alloy phase diagrams: (a) without and (b) with vibrational effects taken into account. Dotted curves indicate metastable phase equilibria. α (β): fcc-(bcc-) based solid solution; α' : LI_2 ; β' : $B2$.

2.7 mRy/atom (3.5 kJ/mole) which lies between two values extracted from experimental data, i.e., 0.97 [17] and 3.4 [3] mRy/atom. The DO_3 at Cu_3Zn is found metastable with respect to LI_2 , whereas at $CuZn_3$ this DO_3 -ordered phase is barely stable. Overall the β -based alloys essentially prevail in the Zn-rich side of the phase diagram, except above 80 at.% Zn. As previously mentioned, the vacancy-induced formation of complex phases originating from the bcc lattice makes our approach a reasonable starting point for further studies on the ternary Cu-Zn- \square .

Second, a domain of stability of α' is predicted at relatively low temperature (below 300 K) which may explain why such long-range order has never been observed experimentally, due to the slow diffusion process. From the

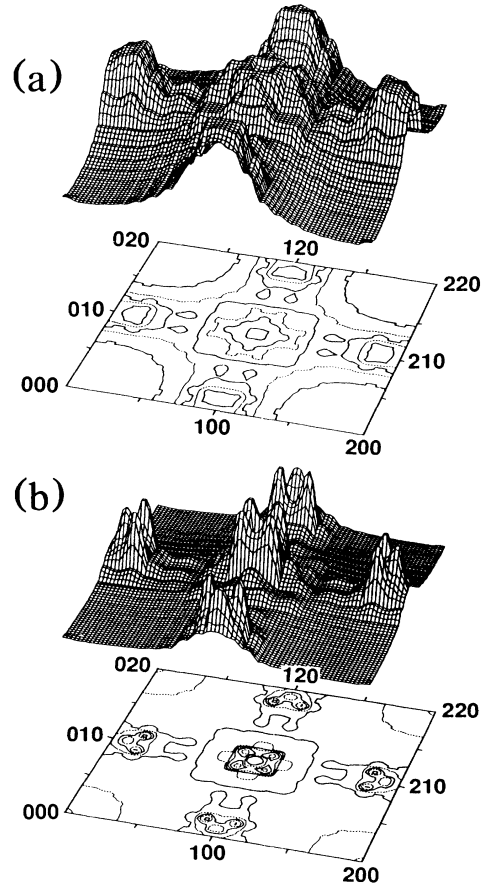


FIG. 3. Calculated SRO diffuse scattering intensity in the (001) plane, at (a) $T/T_c \sim 1.26$ and (b) $T/T_c \sim 1.06$, for a fcc-based $Cu_{80}Zn_{20}$ alloy.

calculated EPIs, one can estimate the antiphase boundary (APB) energy associated with a $\frac{1}{2}a(110)$ displacement every two (001) planes. Such energy translates into an energy difference between LI_2 (α') and the simplest long-period superstructure (LPS), DO_{22} , of Al_3Ti type, and is given by

$$\gamma = (2V_2 - 8V_3 + 16V_4 + \dots)/a^2,$$

where a is the fcc-equilibrium lattice parameter. In Cu_3Zn , γ is only of the order of 12 mJ/m². This strongly indicates that LI_2 is practically degenerate with any LPS described by APBs of the [100] type. The degeneracy is only lifted by weak, long-range interactions, which makes it more appropriate to describe the occurrence of LPS in reciprocal space. Such an alternative is provided by the k -space version of the GPM, namely, the CFT [18]. Short-range-order (SRO) diffuse scattering intensities in the (001) plane calculated with this method are displayed in Fig. 3 for α - $Cu_{80}Zn_{20}$ and $T/T_c \sim 1.26$ and 1.06 (where T_c is the order-disorder temperature). Diffuse peaks at about the $[1\frac{1}{4}0]$ positions in reciprocal space strongly suggest the existence of a LPS of DO_{23} type. This result confirms previous theoretical predictions [19],

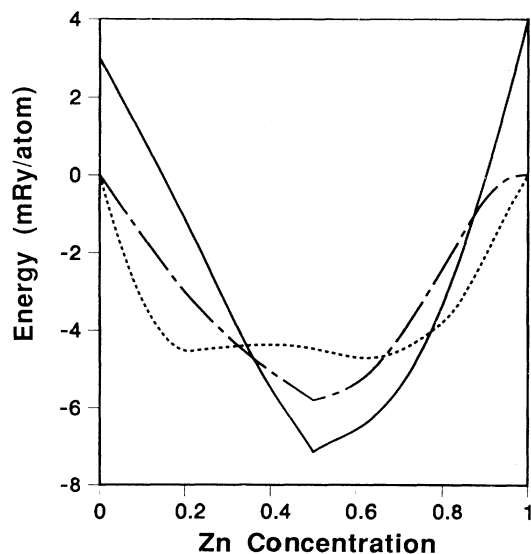


FIG. 4. Internal energy (in mRy/atom) vs Zn concentration for LI_2 (dotted curve), LI_0 (dashed-dotted curve), and $B2$ (solid curve), at $T=0$ K.

and the more recent findings from neutron diffuse scattering [4]. Figure 3(b) shows that additional splitting of the diffuse peaks occurs near T_c , a result which would be interesting to confirm experimentally.

Finally, as indicated in Fig. 2, a metastable LI_0 phase is found with a low T_c of about 288 K. The zero-temperature internal energies for the three ordered phases LI_2 , LI_0 , and $B2$, calculated as a function of concentration, are shown in Fig. 4. These results strongly support the fact that a diffusionless martensitic transformation may occur, in a narrow range of composition around 40 at. % Zn, between $B2$ and LI_0 . This displacive transformation originates from a softening of the first nn EPI in the bcc phase [see Fig. 1(b)] in this same range of composition. Our calculations show that β' is barely stable at low temperature, and its stability at elevated temperature is mainly due to favorable contribution of its vibrational and configurational entropies to the total free energy, as discussed in [6]. Our study suggests a rather low value of the characteristic temperature of the martensitic transformation M_s , in a narrow range of composition around 40 at. % Zn, as observed experimentally [3].

In summary, the first-principles approach used throughout this work produces remarkably accurate results and predictions on order-disorder phenomena. It also provides information on structural transformation as well as on the relative stability and metastability of various ordered configurations. All the results were derived solely from the knowledge of the electronic structure of a random medium. Our study reveals the role played by vibrational properties in stabilizing β -brass at high temperature. Extension of this work to other "electronically driven" Hume-Rothery phases will allow us, in the near future, to fully corroborate the ideas developed sixty

years ago on a phenomenological basis, and also to apply our present methodology and predictive capabilities to other materials of technological importance.

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