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# Ordered Phases in $Cu_2NiZn$: A First-Principles Monte Carlo Study

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Monte Carlo simulations based on effective interactions obtained from first-principles calculations reveal the existence of *three* ordered phases in ternary $Cu_2NiZn$: (i) "modified"-$L1_0$ (0–600 K), (ii) $L1_2$ (600–850 K), and (iii) $L1_0$ (850–1200 K). This is in contrast to the generally accepted picture which assumes the existence of only *two*. We demonstrate that this sequence of phases is a consequence of the symmetry of the ground state and the magnitude of the dominating pair interactions. It agrees with available experimental data. [S0031-9007(98)06539-9]

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Many of the alloys used in technological applications are multicomponent systems and may exhibit a number of phase transitions [1] which may destroy their desirable physical properties. A detailed knowledge of possible phase transitions in specific metallic alloys is therefore of vital importance. In this respect the advent of powerful computers has led to a surge in first-principles calculations and subsequent modeling of phase transitions in binary alloys [2] but only to a few studies of ordering in multicomponent systems.

Ternary fcc-based $Cu_2NiZn$ known as "German silver" or "Newsilver" is an alloy of technological interest, which according to the generally accepted interpretation of a large body of experimental investigations [3] undergoes two phase transitions with decreasing temperature: (i) at about 774 K from the disordered fcc solid solution to an $L1_2$ structure and (ii) at about 600 K to a modified $L1_0$ structure. Possibly at variance with this picture of only *two* phase transitions is the observation by Hashimoto *et al.* [4] of an unusually high value of the Ni-Zn short-range order (SRO) parameter in a $Cu_{47}Ni_{49}Zn_{24}$ sample quenched from 870 K, i.e., from above the first phase transition, indicating the existence of a so far undiscovered phase intermediate between the solid solution and the $L1_2$ structure [5].

Recently Althoff *et al.* [6,7] performed a detailed first-principles study of the atomic short-range order in disordered $Cu_{50}Ni_{25}Zn_{25}$ and found that the disordered state became unstable relative to a $\langle 100 \rangle$-type ordering at 985 K using the Onsager cavity-field correction. This temperature is about 200 K higher than the observed order-disorder transition temperature and the predicted high temperature ordered state is an unusual $L1_0$-type structure [8] which is not seen experimentally. In the most recent work Althoff and Johnson [9] neglected the Onsager correction and did not find the $L1_0$-type structure obtained in their previous study. In addition, the transition temperature became even higher, 1200 K. Clearly, further investigations, theoretical as well as experimental, are needed to resolve the question of the phase transitions and ordering in $Cu_2NiZn$.

In the present Letter we provide a description of the phase transitions in $Cu_2NiZn$ formed on the basis of first-principles total energy calculations, Monte Carlo simulations, and an analysis in terms of the concentration wave formalism [10]. According to the latter a complete characterization of $Cu_2NiZn$ must include *four* order parameters [11], and the alloy may exhibit as many three distinct ordering sequences leading from the random phase to the modified $L1_0$ structure involving five differently ordered phases. Our calculations show that only one of the sequences may be found experimentally and, hence, we predict three different phases and *three* phase transitions in $Cu_2NiZn$ in the temperature range below melting.

Our Monte Carlo simulations of ordering in $Cu_2NiZn$ are based on effective cluster interactions (ECI) determined by first-principles total energy calculations, and we take advantage of the order-$N$ locally self-consistent Green's function technique, recently proposed by Abrikosov *et al.* [12,13]. This technique builds on Andersen's linear methods [14,15] and allows us to treat a 144 atom supercell with different atomic configurations of Cu, Ni, and Zn at a *fixed* $Cu_{50}Ni_{25}Zn_{25}$ composition. The calculated equilibrium volume changes less than 0.3% during ordering and all calculations [16] are therefore performed at a fixed volume of 311.8 ($bohr^3$/unit cell). Lattice relaxation effects are small [17] and neglected in the present calculations. The interactions obtained by the present procedure are *concentration dependent* in contrast to the standard Connolly-Williams treatment [18] in terms of *concentration-independent* interactions. As a result, there is a substantial reduction in computational efforts due to the reduction of the number of significant multisite interactions [19].

The calculated total energies of 32 suitably chosen alloy configurations are mapped onto a cluster expansion of the total energy of the configuration defined by the

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probabilities $P_j^{\alpha\beta}$ to find pairs of atomic species $\alpha$ and $\beta$ separated by $j$ coordination shells

$$E = E_{\text{rand}} + \sum_{\alpha\neq\beta;j} D_j(c_\alpha c_\beta - P_j^{\alpha\beta})V_j^{\alpha\beta}. \quad (1)$$

Here, $E_{\text{rand}}$ is the total energy of the completely random alloy, $V_j^{\alpha\beta}$ the corresponding ECI, $D_j$ the degeneracy factor, and $c_X$ the concentration of element X in the alloy. A least-squares fit is used to extract 21 concentration- and volume-dependent ECI, corresponding to pair interactions up to the seventh coordination shell. The so determined cluster expansion reproduces the first-principles total energies with an average error of 0.014 mRy with the maximum error not exceeding 0.2 mRy. Subsequent tests for the structures not included in the fit show that the error of the expansion never exceeds 0.22 mRy, i.e., about 4% of the ordering energy.

The extracted ECIs are presented in Fig. 1 and we note that the nearest-neighbor interactions are large and positive indicating a tendency to order in pairs of atoms in the system. The magnitude of the pair ECI decreases from NiZn over CuZn to CuNi as expected from the values in the corresponding binary systems. In fact, it is this succession of pair interactions which determines the sequence of phase transitions in $Cu_2NiZn$ predicted by the calculations to be presented.

The Monte Carlo simulations are performed for a cubic box containing 32 000 atoms on an fcc lattice using periodic boundary conditions. They include slow cooling with long simulated annealing at each particular temperature and further averaging of the thermodynamic values on the basis of 3000 Monte Carlo steps. The results are presented in Fig. 2 where we show the unit cells of the predicted stable crystal structures, the average occupation numbers of Cu, Ni, and Zn on the three inequivalent sublattices, and the values of the four order parameters as obtained in the temperature range 100–1500 K.

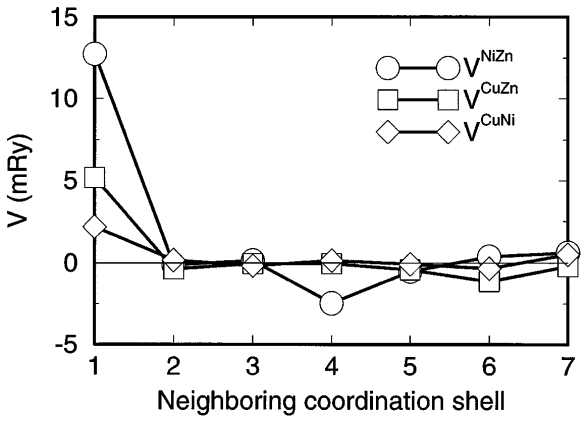


FIG. 1. The calculated effective Ni-Zn, Cu-Zn, and Ci-Ni interactions in $Cu_2NiZn$ for the first seven coordination shells as given by Eq. (1).

The variation of the calculated occupation numbers with temperature clearly exhibits three phase transitions in the range from the random alloy to the ground state. This corresponds to three ordered phases, two of which have been observed experimentally, i.e., the ground state modified $L1_0$ structure and the partially ordered $L1_2$ structure both with Zn atoms at the corners of the cubic unit cell, and a new high-temperature ordered phase between 850 and 1200 K in the form of the $L1_0$ structure with alternating layers of (Ni, Cu) and (Zn, Cu). The sequence of structures predicted in Fig. 2 is not accidental but an unavoidable consequence of the symmetry of the ground state, the number of components in the system, and the succession of the effective pair interactions in the system [20].

The results of the simulations may easily be analyzed within concentration wave theory [10] and for this purpose we observe that the ordering in $Cu_2NiZn$ is generated

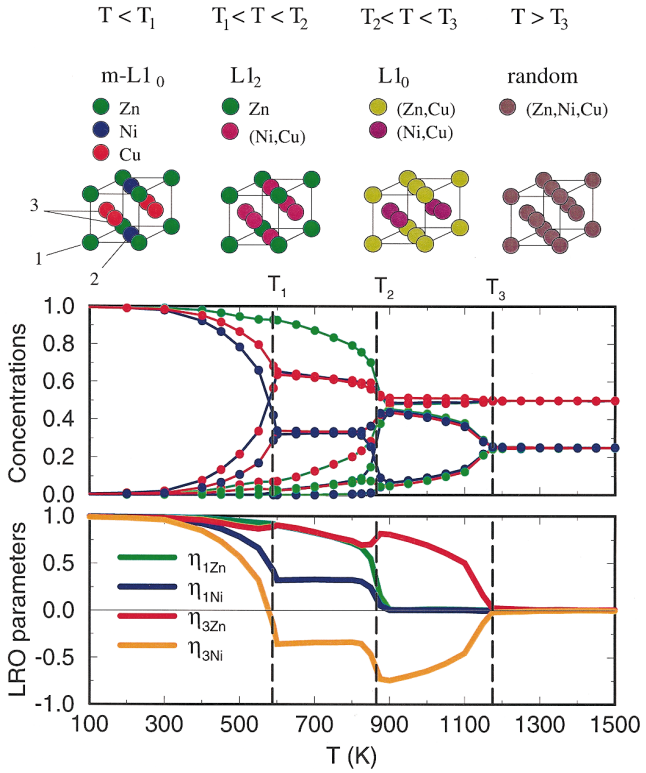


FIG. 2(color). Monte Carlo simulations of the ordered phases in $Cu_2NiZn$ predicting phase transitions from the ground state, which is a modified $L1_0$ structure, through a partially ordered $L1_2$ structure over an $L1_0$ structure to the disordered fcc solid solution. The actual structures are depicted in the upper panel. In the middle panel we show the Gibbs averages of the occupation numbers on the sublattices. Here, solid circles of green, blue, and red colors correspond to Zn, Ni, and Cu atomic species, respectively, while lines of green, blue, and red colors connecting the circles correspond to the first, second, and third sublattices, respectively, defined in the upper panel. In the lower panel we show the long-range order (LRO) parameters given by Eqs. (2) and (3)

by the $\langle 100 \rangle$ star which has three branches $\mathbf{k}_1 = \frac{2\pi}{a}[100]$, $\mathbf{k}_2 = \frac{2\pi}{a}[010]$, and $\mathbf{k}_3 = \frac{2\pi}{a}[001]$ of the concentration wave of the alloy components. Here, $a$ is the lattice parameter. Further, there are only two independent occupation numbers for each sublattice and since Zn and Ni show the largest tendency towards ordering we use the Gibbs averages of the occupation numbers for these two components at the atomic positions $\mathbf{R}$ of the fcc underlying lattice to describe the concentration wave, i.e.,

$$n_{\mathrm{Zn}}(\mathbf{R}) = c_{\mathrm{Zn}} + \frac{1}{4}\left(\eta_{1\mathrm{Zn}}[e^{i\mathbf{k}_1\cdot\mathbf{R}} + e^{i\mathbf{k}_2\cdot\mathbf{R}}] + \eta_{3\mathrm{Zn}} e^{i\mathbf{k}_3\cdot\mathbf{R}}\right), \quad (2)$$

$$n_{\mathrm{Ni}}(\mathbf{R}) = c_{\mathrm{Ni}} + \frac{1}{4}\left(\eta_{1\mathrm{Ni}}[-e^{i\mathbf{k}_1\cdot\mathbf{R}} - e^{i\mathbf{k}_2\cdot\mathbf{R}}] + \eta_{3\mathrm{Ni}} e^{i\mathbf{k}_3\cdot\mathbf{R}}\right). \quad (3)$$

In these expressions $c_{\mathrm{Zn}}$ and $c_{\mathrm{Ni}}$ are the concentrations of Zn and Ni in the alloy and $\eta_{iX}$ the *four* independent long-range order parameters for different branches $\mathbf{k}_i$ dictated by the symmetry of the ground state and uniquely defining all the possible long-range ordered states in the alloy. Further, $\mathbf{k}_3$ is the branch which separates the Cu atoms from Zn and Ni, and $\mathbf{k}_1$ and $\mathbf{k}_2$ are the branches which separate the Zn and Ni atoms.

We now discuss the evolution predicted by the simulations of the system from the disordered state above 1200 K where all $\eta_{iX} = 0$ and all atoms are randomly distributed between sublattices to the ground state where all $\eta_{iX} = 1$ and the atoms are completely ordered on the sublattices. The first phase transition occurs at about 1200 K when the Ni-Zn interactions become sufficiently strong to overcome the configurational entropy and establish long-range order. The transition takes place between the disordered solid solution and a partially ordered (Zn, Cu) (Ni,Cu)-$L1_0$ structure, where Ni and Zn atoms are ordered in the usual $L1_0$ structure, while Cu atoms, which have weak interactions with Zn and Ni, distribute themselves almost equally between all the sublattices with a very weak preference for Ni sites ($\eta_{3\mathrm{Zn}} > -\eta_{3\mathrm{Ni}}$) due to stronger Cu-Zn interactions (see the middle panel of Fig. 2). For this structure we have in general $\eta_{1\mathrm{Zn}} = \eta_{1\mathrm{Ni}} = 0$ and $0 < \eta_{3\mathrm{Zn}}, -\eta_{3\mathrm{Ni}} < 1$.

The second phase transition occurs at approximately 850 K and is caused by the Cu-Zn interactions intermediate in magnitude between the strong Ni-Zn and the weak Cu-Ni interactions. Since both the Ni-Zn and the Cu-Zn interactions participate in establishing long-range order and the Cu-Ni interactions do not, Zn occupies preferentially one sublattice while Cu and Ni are equally distributed between the remaining sublattices. This is the $(\mathrm{Ni}, \mathrm{Cu})_3$Zn-$L1_2$ structure, where the LRO parameters obey the following rules: $0 < \eta_{1\mathrm{Zn}} = \eta_{3\mathrm{Zn}} < 1$ and $0 < \eta_{1\mathrm{Ni}} = -\eta_{3\mathrm{Ni}} < \frac{1}{3}$. Further, since the Ni-Zn interaction is the strongest in $Cu_2NiZn$ there are practically no Ni atoms on the sublattice which is preferentially occupied by Zn atoms and therefore $\eta_{1\mathrm{Ni}} = -\eta_{3\mathrm{Ni}} \approx \frac{1}{3}$. Note that this transition results in an *increase* in lattice symmetry from tetragonal $L1_0$ to cubic $L1_2$ as the temperature decreases. This is most unusual for transformations involving comparable ordered phases [1].

At about 600 K the system undergoes the third phase transition to the modified $L1_0$ ordered structure where each of the three inequivalent sublattices is occupied by either Zn, Ni, or Cu atoms. Here, the important factor is the ordering tendency between Cu and Ni atoms. It is easy to show that if there were a tendency towards segregation as in the binary Cu-Ni system then the Monte Carlo simulations would not have the modified $L1_0$ structure as the ground state. In other words, the weak but attractive Cu-Ni interaction in $Cu_2NiZn$ stabilizes the modified $L1_0$ structure.

In the comparison of our results with the experimental data we find very good agreement in regard to the temperatures of the second and third phase transitions and support for the identification of the ordered phase between 600 and 774 K as the $L1_2$ ordered structure. The existence of the high temperature $L1_0$ structure, i.e., the phase below the first phase transition, as predicted by the present Monte Carlo simulations, is seemingly in contradiction to the conclusion drawn from the experimental investigations that $Cu_2NiZn$ should be a disordered alloy in this temperature range and thus only exhibit two phase transitions. However, closer inspection of the available experimental data reveals that there is no solid basis for this conclusion.

The only reliable experimental data concerning the configurational states above the second phase transition is the determination of the short-range order parameters by Hashimoto *et al.* [4] based on measurements of the anomalous scattering of synchrotron radiation on a sample quenched from 870 K. As has already been noticed by Althoff *et al.* [7] the values for the SRO parameters obtained in Ref. [4] in fact suggest long-range order in the system. To address this question we have calculated the Fourier transforms of the Warren-Cowley SRO parameters related to the measured partial intensities and we find that the overall ratios of the peak heights of Ni-Zn, Cu-Zn, and Cu-Ni SRO at $\mathbf{k} = \frac{2\pi}{a}[100]$ obtained by Hashimoto *et al.* are very close to those we obtain for the $L1_2$ ordered state in the temperature range 800–850 K. Thus, the experimental study of the high-temperature region appears to be incomplete and further careful investigations would be of great interest.

In summary, we have performed Monte Carlo simulations of the ordering in $Cu_2NiZn$ and combined this with an analysis based on the concentration wave formalism. We find that the previously proposed identification of the two low temperature phases as "modified" $L1_0$ and $L1_2$ are consistent with our results. We further predict the existence of a new ordered state, namely, a partially ordered (Zn, Cu) (Ni, Cu)-$L1_0$ phase, and show that the states found in the Monte Carlo simulations and the

sequence in which they order are direct consequences of the relative magnitudes of the interactions between the alloy components. The ordering tendency between Cu and Ni atoms is found to be a necessary factor in stabilizing the observed ground state in $Cu_2NiZn$.

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[17] This is discussed, for instance, in Ref. [4]. Note that Ni, Cu, and Zn are neighbors in the same row of the periodic table and accordingly the size mismatch between them is very small. It has further been shown theoretically [N. Papanikolaou, R. Zeller, P. H. Dederichs, and N. Stefanou, Phys. Rev. B **55**, 4157 (1997)] that the contribution to the energetics of single impurities of Ni and Zn in Cu caused by local relaxations is practically negligible.

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[19] We have estimated the interactions in $Cu_2NiZn$ on the basis of the generalized perturbation method (GPM). This shows that already three-site interactions are very small and give a negligible contribution to the the ordering energy of the ground state. At the same time concentration independent multisite interactions should be quite big in this system due to the strong concentration dependence of the *pair* interactions (see Ref. 7).

[20] Another succession of the effective pair interactions could result in other partially ordered phases $L1_2'$ [of type $(Cu, Ni)_3(Zn, Ni)$] and $L1_2''$ (of type $Cu_3(NiZn)$].