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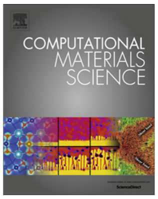

CPA descriptions of random Cu-Au alloys in comparison with SQS approach

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ABSTRACT

The lattice constant, formation enthalpy, and elastic parameters of $Cu_{1-x}Au_x$ ($0 \leqslant x \leqslant 1$) alloys in the face centered cubic crystallographic phase are investigated by using the first-principles exact muffin-tin orbitals and plane-wave pseudopotential methods in order to explore the effect of alloying with special focus on the impact of local lattice distortion (LLD) on the above properties. The compositional disorder is treated within the framework of the coherent potential approximation (CPA) and the special quasi-random structure (SQS) scheme. Calculations based on SQS and CPA show that, while LLD lowers significantly the formation enthalpy of $Cu_{1-x}Au_x$ due to the large size mismatch between Cu and Au atoms, it has negligible influence on the lattice constants and elastic parameters. These findings confirm the reliability of CPA for computing the enthalpy changes upon isotropic and unisotropic lattice distortions in disordered alloys with sizable atomic size differences.

1. Introduction

Coherent potential approximation (CPA) formulated in the framework of multiple scattering theory [1–3] provides an elegant way to describe the compositional and magnetic disorder in random solid solutions. In combination with first-principles methods using the Green function technique to solve the Kohn-Sham equation, especially the one employing the Exact Muffin-Tin Orbitals (EMTO) method and the full-charge density technique [4–7], CPA has been successfully applied to calculate the bulk properties (*e.g.*, lattice constant, elastic modulus, and stacking fault energy) of many disordered systems such as steel alloys, Ni based alloys, Al-Li alloys, Heusler alloys, and high entropy alloys [8–18]. Within CPA, a coherent Green function is constructed as the composition weighted average of the individual Green functions of the alloy components. These, in turn, are obtained by solving the impurity problem within the single-site approximation. Hence, one may take a very small unit cell that retains the high symmetry of the underlaying lattice to treat any arbitrary compositions, and, therefore, very low computational load is required. This greatly facilitates the high-throughout first-principles calculations of materials. However, the single-site CPA is frequently criticized for not being able to take into account the local lattice distortion (LLD) induced by solutes. Therefore, when employing CPA one should be able to estimate the impact of LLD on the properties in question and whether this error could override the chemical effects.

Special Quasi-random Structure (SQS) [19,20] is another approach that can take care of the composition disorder present in solid solutions. The idea of SQS is to construct a special supercell for which the atomic correlation functions mimic those of the physically most relevant ones of the perfectly random solid solutions. Within the supercell, the atomic positions can be relaxed through minimizing the interatomic Hellmann-Feynman forces so that the LLD effect induced by local chemical environment is properly considered. The disadvantage of SQS is that large supercell is needed for multi-component systems and the symmetry of the supercell is generally lower than that of the underlying lattice making the calculations often cumbersome.

The LLD effects have been examined by comparing the CPA and SQS calculations for some particular systems [21–23]. The calculations by Alling et al. [21], demonstrated that the mixing energy of cubic $Ti_{1-x}Al_xN$ from CPA and unrelaxed SQS calculations are in

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good agreement with each other whereas the relaxed SQS calculations drops it by about 30%, but the trend against the composition x remains unchange. The magnetic properties of FeCr and CrN from CPA and SQS calculations have been compared by Tarafder et al. [22] and Alling et al. [23], respectively, and reasonable agreement was found.

The physical properties (*e.g.*, lattice constant, mixing energy, elastic constants, magnetism) of different systems (*e.g.*, with mismatches in atomic size, magnetic behavior or electronic configuration) may exhibit various sensitivities to LLD. Hence a systematic evaluation of the LLD effect on basic properties is greatly appreciated to verify the CPA calculations. Such assessments become accessible only recently when CPA, as implemented, *e.g.*, in the EMTO method [4–7], turned out to be robust enough to provide data with accuracy comparable to that obtained using SQS in combination with advanced full-potential techniques. In a recent work [24], we investigated the LLD effects on the lattice constants, mixing energy, and elastic constants of random face-centered cubic (fcc) $\text{Ti}_{1-x}\text{Al}_x$. The Ti-Al system was selected as a prototypic binary alloy where the components have similar atomic sizes (the experimental Wigner-Seitz radii for Al and Ti differ by $\sim 2\%$) but very different valence electron configurations. We showed that for fcc-$\text{Ti}_{1-x}\text{Al}_x$, CPA performs well for all computed physical parameters and the LLD has a negligible influence on them. In the present work, we choose fcc-$\text{Cu}_{1-x}\text{Au}_x$ alloy considering that Cu and Au have similar electron configurations but very large atomic size mismatch. Actually, the experimental Wigner-Seitz radii for Cu and Au differ by $\sim 13\%$, placing this binary system close to the Hume-Rothery empirical upper limit for solid solution formation [25]. Here we carry out parallel CPA and SQS calculations in order to check the performance of CPA and establish the LLD effect on the aforementioned properties in the case of fcc-$\text{Cu}_{1-x}\text{Au}_x$.

The rest of the paper is organized as follows. In Section 2, the theoretical framework is provided including the numerical details of the calculations and an overview of the CPA and SQS techniques. In Section 3, we present results obtained for the lattice parameter, formation enthalpies and elastic constants of $\text{Cu}_{1-x}\text{Au}_x$ random alloys. A short discussion of the calculated trends is given in Section 4. We summarize our work in Section 5.

2. Computational method

2.1. Total energy calculations

We performed total-energy calculations in the framework of Density Functional Theory (DFT) using the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE) [26] for the exchange-correlation functional. The adopted first-principles techniques are the EMTO method [4–7] and Projector Augmented Wave (PAW) method [27,28] as implemented in the Vienna Ab initio Simulation Package (VASP) [29–31].

The EMTO theory is an improved screened Korringa-Kohn-Rostoker (KKR) method [32], where the exact one-electron potential is represented by large overlapping muffin-tin potential spheres. By using overlapping spheres one describes more accurately the exact crystal potential, when compared with the conventional muffin-tin or not overlapping approaches [6,33]. The EMTO method has been successfully applied in the *ab initio* calculations of the ground state properties of ordered and disordered alloys [8–12,34,35]. In EMTO calculations, the disorder is treated within CPA [1–3], and the full charge density (FCD) technique [36,37] is implemented for accurate total energies.

In the present application to Cu-Au system, the basis set included s, p, d and f orbitals ($l_{max} = 4$) and the l-cutoff for the charge density was chosen as $l^h_{max} = 8$. The k-point convergence was carefully tested and finally we chose $29 \times 29 \times 29$ k-points mesh in the irreducible part of the Brillouin zone. The Green function was calculated for 16 complex energy points distributed exponentially on a semicircular contour including the valence states. The electrostatic correction to the single-site approximation was described using the screened impurity model with a screening parameter of 0.9 [38].

Parallel with the EMTO-CPA calculations, we carried out two series of SQS calculations by the PAW-VASP method [28]. First, we omitted the LLD in all VASP-SQS calculations, and second we performed locally relaxed calculations by accounting properly for the LLD effects. The disordered supercell structures of $\text{Cu}_{1-x}\text{Au}_x$ $(0 \leqslant x \leqslant 1)$ were generated by the Monte Carlo algorithm [39] using 32-atom supercells $(2 \times 2 \times 2)$. We also tested larger supercells and their effect on computed physical properties. For instance, the calculated formation enthalpies of the 32 and 96-atom SQSs differ by 1.3 meV/atom for unrelaxed structures and by 0.7 meV/atom for fully relaxed structures. Based on that, we decided to present results only for the 32-atom SQS and consider the above deviations as the typical error bar associated with the size of the supercell. The VASP calculations were performed using an energy cutoff of 400 eV for the plane wave basis set. The integration over the Brillouin zone was done using a $10 \times 10 \times 10$ grid of special k-points determined according to the Monkhorst-Pack scheme [40]. The convergence tolerance for the total energy was set as 1×10^{-6} eV, and 10^{-2} eV/Å for the Hellmann-Feynman forces during ionic relaxations. The volumes of all SQS supercells were optimized but the shapes were kept fixed. At this point we should note that the stresses acting on the cubic SQS supercell were calculated to be very small, meaning that the deviation of the fully-relaxed SQS supercell from the volume-relaxed cubic SQS supercell should be negligible. Our test calculations fully support this expectation. Namely full relaxation of the supercell yielded volume and elastic constants in very good agreement (within the typical numerical errors) with those calculated using fixed shape.

In addition to PBE, we also performed some EMTO-CPA calculations employing the recent Quasi Non-Uniform Approximation (QNA). Details about QNA can be found in Refs. [41,42]. Comparing the PBE and QNA results, one can learn about the effect of exchange-correlation approximation on the formation enthalpy of random Cu-Au system.

2.2. Elastic parameters

The elastic properties of single-crystals are described by the elements C_{ij} of the elasticity tensor. For cubic systems, there are three independent elastic constants: C_{11}, C_{12} and C_{44}. Often C_{11} and C_{12} are derived from the tetragonal shear elastic constant $C' = (C_{11} - C_{12})/2$ and the bulk modulus $B = (C_{11} + 2C_{12})/3$.

In EMTO calculations, first the theoretical equilibrium volume and the bulk modulus were determined from an exponential Morse-type function [43] fitted to the *ab initio* total energies of fcc structures calculated for nine different atomic volumes. All elastic constant calculations were performed at the corresponding theoretical equilibrium volumes. The cubic elastic constants were computed according to the energy-strain relation $(\Delta E \sim \varepsilon^2)$. We used volume-conserving orthorhombic and monoclinic deformations, *viz.*

$$\begin{pmatrix} 1+\varepsilon_o & 0 & 0 \\ 0 & 1-\varepsilon_o & 0 \\ 0 & 0 & 1/(1-\varepsilon_o^2) \end{pmatrix}, \tag{1}$$

and