Density Functional Study of Elastic Properties of Metallic Alloys

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Abstract

Special quasi-random structure (SQS) and coherent potential approximation (CPA) are techniques widely employed in the first-principles calculations of random alloys. The aim of the thesis is to study these approaches by focusing on the local lattice distortion (LLD) and the crystal symmetry effects. We compare the elastic parameters obtained from SQS and CPA calculations. For the CPA and SQS calculations, we employ the Exact Muffin-Tin Orbitals (EMTO) method and the pseudopotential method as implemented in the Vienna Ab initio Simulation Package (VASP), respectively. We compare the predicted trends of the VASP-SQS and EMTO-CPA parameters against composition.

As a first case study, we investigate the elastic parameters of face centered cubic (fcc) Ti$_{1-x}$Al$_x$(0≤x≤100 at.%) random solid solutions as a function of Al content (x). The EMTO-CPA and VASP-SQS results are in good agreement with each other. Comparing the lattice constants from SQS calculations with and without local lattice relaxations, we find that in Ti-rich (Al-rich) side the lattice constants remain almost unchanged (slightly increase) upon atomic relaxations. Taking local lattice distortions into consideration decreases the $C_{11}$ and $C_{44}$ elastic parameters, but their trends are not significantly affected. The $C_{12}$ elastic constant, on the other hand, is almost unchanged when atomic relaxations are included. In general, the uncertainties in the elastic parameters associated with the symmetry lowering in supercell studies turn out to be superior to the differences between the two alloy techniques including the effect of LLD.

We also investigate the elastic properties of random fcc Cu$_{1-x}$Au$_x$(0≤x≤100 at.%) alloys as a function of Au content employing the CPA and SQS approaches. It is found that the CPA and SQS values for $C_{11}$ and $C_{44}$ are consistent with each other no matter whether the atomic relaxations are taken into account or not. On the other hand, the EMTO-CPA values for $C_{44}$ are slightly larger than those from SQS calculations especially for Cu-rich alloys which we ascribe to the differences in the DFT solvers rather than the differences between CPA and SQS.

The Perdew-Burke-Ernzerhof (PBE) approximation to the exchange-correlation term in density functional theory (DFT) is a mature approach and have been adopted routinely to investigate the properties of metallic alloys. In most of the cases, PBE provides theoretical results in good agreement with experiments. However, the ordered Cu-Au system turned out to be a special case where large deviations between the PBE predictions and observations occur. In this work, we make use of a recently developed exchange-correlation functional, the so-called quasi-non-uniform exchange-correlation approximation (QNA), to calculate the lattice constants and formation energies for ordered Cu-Au alloys as a function of composition. The
calculations are performed using the EMTO method. We find that the QNA functional leads to excellent agreement between theory and experiment. The PBE strongly overestimates the lattice constants for ordered Cu3Au, CuAu, CuAu3 compounds and also for the pure metals which is nicely corrected by the QNA approach. The errors in the formation energies of Cu3Au, CuAu, CuAu3 relative to the experimental data decrease from 38-45% obtained with PBE to 5-9% calculated for QNA.