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Calculating elastic constants in high-entropy alloys using the coherent potential approximation: Current issues and errors

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ABSTRACT

The new class of high-entropy alloys (HEAs) materials have shown interesting properties, such as high strength and good ductility. However, HEAs present a great challenge for conventional *ab initio* calculations and the few available theoretical predictions involve a large degree of uncertainty. An often adopted theoretical tool to study HEAs from first-principles is based on the exact muffin-tin orbitals (EMTO) method in combination with the coherent potentials approximation (CPA), which can handle both chemical and magnetic disorders. Here we assess the performance of EMTO-CPA method in describing the elastic properties of HEAs based on Co, Cr, Fe, Mn, and Ni. We carefully scrutinize the effect of numerical parameters and the impact of various magnetic states on the calculated properties. The theoretical results for the elastic moduli are compared to the available experimental values.

1. Introduction

In the process of investigating the unexplored central region of the multi-component alloys space, Cantor et al. surprisingly found that the equi-molar CoCrFeMnNi alloy forms a single phase solid solution with face centered cubic (fcc) structure [1]. Motivated by the novel design concept of high-entropy alloys (HEAs) proposed by Yeh et al. [2], a large number of experimental works focused on the microstructural and mechanical properties the fcc Co–Cr–Fe–Mn–Ni based HEAs [3–12].

All five components of CoCrFeMnNi HEA are magnetic in their ground state: Fe, Co and Ni are ferromagnetic (FM), Mn has a multi-magnetic state, and Cr is antiferromagnetic (AM). Their equi-molar composition is paramagnetic (PM) at room temperature. The related HEAs show rather different magnetic behaviors [8–10]. Zhang et al. [8] studied the ferromagnetic state of CoFeNi. Lucas et al. [9,10] used the vibrating sample magnetometry to determine the high-temperature magnetic applications of HEAs and investigated the change of magnetic behavior with increasing temperature. To our knowledge, the magnetic properties of CoCrFeMnNi and their influence on the structural and mechanical properties have not yet been studied by dedicated experiments. In the case of theoretical modeling, limited works [13,14] focused on the high-entropy alloys due to the complicated chemical and magnetic disorder. As a powerful tool which allows one to treat substitutional solid solutions, the coherent potential approximation (CPA) has been used to successfully predict the equilibrium bulk properties of some HEAs [15–18]. Despite of the intrinsic *ab initio* nature, calculation details may also produce a sizable effect on the calculated equilibrium volume and elastic parameters [15,16]. Therefore, establishing a robust *ab initio* toolkit with all necessary numerical approximations to the present problem is very important and timely to extend the scope of theoretical modeling of HEAs. In light of that, here we employ the *ab initio* exact muffin-tin orbitals method in combination with the coherent potential approximation (EMTO-CPA) [19] to investigate the phase stability and magnetic states of CoFeNi, CrFeNi, CoCrFeNi and CoCrFeMnNi HEAs, to study the effect of magnetism on the equilibrium volume and elastic properties, and to reveal the changes in the elastic properties induced by gradually increasing the number of alloying elements.

In the following section, first we assess two possible calculation schemes in the EMTO-CPA method. Then we discuss the phase

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stability and equilibrium properties derived from different calculation schemes. Finally we give a detailed comparison between the theoretical and experimental Young's moduli.

2. Theoretical methodology

2.1. The ab initio tool

The EMTO method [19] is an efficient *ab initio* approach for solving the Kohn–Sham equations [20]. The CPA is a powerful technique which is used to treat the substitutional disorder both for chemical and magnetic degrees of freedom [21,22]. In the present EMTO-CPA calculations, the Perdew–Burke–Ernzerhof (PBE) exchange–correlation density functional [23] was used to calculate the charge density and total energy. We employed the s, p, d, and f states to treat the EMTO basis set. We used 240 (343) inequivalent k points in the irreducible wedge of the fcc (hcp) Brillouin zone, which ensured a relative accuracy $\sim 10^{-2}$ mRy/atom in the total energy differences. The Greens function was calculated for 24 complex energy points around the valence states. The electrostatic correction to the single-site CPA was described using the Screened Impurity Model (SIM) [24,25]. The screening parameters will be discussed in the following section. The core states were treated in two different schemes: soft-core (recalculated after each iteration) and frozen-core (kept at the atomic level). Based on our experience, the frozen-core calculations usually increase the equilibrium volume and thus employing this scheme can give an indication about the volume effect on the calculated properties. The potential sphere radii were chosen to be equal to the corresponding average atomic sphere radius for all alloy components. We neglect all thermal contributions in the present calculations. For the description of paramagnetic HEAs, we employed the disordered local magnetic moment (DLM) picture [27]. The DLM model was shown to describe the random distribution of the local magnetic moments of the paramagnetic state of metals above the magnetic transition temperature [28–30]. Note that the short-range order of the magnetic moments is neglected in the DLM model. The elastic constants were calculated from the strain derivative of the total energy and the polycrystal elastic moduli were obtained via the Voigt–Reuss–Hill averaging method [31]. For further details of the EMTO-CPA calculations, readers are referred to Ref. [19].

2.2. Assessing the single-site approximation for HEAs

Since CPA is a single-site approximation, no information is provided about the charge redistribution around the impurities embedded in the coherent potential effective medium. The problem was proposed to be solved in an approximate way by the so called Screened Impurity Model [24,25]. According to that model, the correction to the electrostatic energy and potential is controlled by the SIM parameters. Here we use the original version of SIM where for all alloy components [26], the same SIM parameter α is assumed. Performing a set of *ab initio* calculations with different α values, we estimate the effect of single-site approximation on the equilibrium bulk properties of the present HEAs. Table 1 lists the Wigner–Seitz (WS) radius w, bulk modulus B and local magnetic moments μ of PM CrFeNi, CoCrFeNi, and CoCrFeMnNi HEAs as a function of α. With increasing α (from 0.602 to 0.902), the local magnetic moments for Fe slightly decrease, whereas μ_{Mn} increases from 1.30 to 1.46μ_B. Nevertheless, the equilibrium w and B are consistent with each other for different α parameters. The largest change for w is 0.003 Bohr ($\sim 0.1\%$) and that for B is 3.1 GPa ($\sim 1.5\%$). Thus one may conclude that the bulk parameters of the present HEAs are not sensitive to the details how the electrostatic correction to the single-site approximation is treated.

In Fig. 1, we show the equilibrium w, the bulk modulus B and the magnetic moments μ as a function of α for FM CrFeNi and CoFeNi HEAs, respectively. For CrFeNi, the total magnetic moment is $\mu_{\mathrm{tot}} = 0.45 - 0.48\mu_B$, and the local magnetic moments are $\mu_{\mathrm{Cr}} = -(0.62 - 0.67)\mu_B, \mu_{\mathrm{Fe}} = 1.87 - 1.89\mu_B$, and $\mu_{\mathrm{Ni}} = 0.16 - 0.18\mu_B$ for $\alpha = 0.602 - 0.902$. Similar effects are found for CoFeNi as well. The changes in w and B are of the same level as those found for the PM alloys (Table 1). Hence the FM results confirm our previous conclusion found for PM alloys, namely the α SIM parameter has negligible effect on the equilibrium bulk properties for the present HEAs.

Parallel to the soft-core calculations, we also performed a set of frozen-core test calculations. These results are shown in Table 2. It is found that α has vanishing effect on the equilibrium parameters of PM CrFeNi and FM CoFeNi HEAs calculated using the frozen-core scheme, although the magnetic moments change slightly. For CoFeNi, the frozen-core $w = 2.660$ Bohr is consistent with the experimental value ($w = 2.658$ Bohr), whereas the calculated total magnetic moment 1.69μ_B is slightly larger than the one reported in experiments (1.30μ_B) [8]. Taking into account the weak α dependence of the bulk parameters and in order to be consistent with the previous works [15,32], in the following we use $\alpha = 0.602$ in connection with EMTO-CPA soft-core calculations, and $\alpha = 0.902$ for EMTO-CPA frozen-core calculations. We notice, however, that allowing for atom-dependent CPA parameters might slightly alter the above results. Furthermore, the actual values of the CPA parameters become very important for the formation enthalpy (not shown). Unfortunately, for the present multi-component alloys it is extremely difficult to generate optimal CPA parameters because of the difficulties associated with modeling the HEAs using standard supercell techniques. Work in this direction is in progress.

2.3. Soft-core versus frozen-core scheme

In the EMTO-CPA method, the soft-core and frozen-core schemes are often used to calculate equilibrium bulk properties and elastic properties. The equilibrium properties obtained from the soft-core calculations are generally in good agreement with the low-temperature experimental values for pure metals [19] and some alloys. However, the soft-core scheme is known to

Table 1
Equilibrium bulk properties of paramagnetic (PM) CrFeNi, CoCrFeNi, and CoCoFeMnNi HEAs listed as a function of the SIM parameter α adopted in EMTO-CPA soft-core calculations. Shown are the Wigner–Seitz radius w (Bohr), the bulk modulus B (GPa), and the local magnetic moments μ_i (μ_B) for alloying elements (i = Fe, Mn). The vanishing local magnetic moments are not shown.

α	CrFeNi			CoCrFeNi			CoCrFeMnNi			
	w	B	μ_{Fe}	w	B	μ_{Fe}	w	B	μ_{Fe}	μ_{Mn}
0.602	2.621	195.0	1.66	2.607	207.0	1.79	2.606	186.2	1.56	1.30
0.702	2.621	195.3	1.65	2.605	203.9	1.76	2.606	184.5	1.56	1.35
0.802	2.620	195.3	1.63	2.604	204.3	1.77	2.605	184.2	1.56	1.39
0.902	2.619	194.4	1.59	2.604	204.6	1.77	2.605	183.7	1.55	1.46