Editor's Choice

Ab initio calculations of the lattice parameter and elastic stiffness coefficients of bcc Fe with solutes

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ABSTRACT

We present an efficient methodology for computing solute-induced changes in lattice parameters and elastic stiffness coefficients C_{ij} of single crystals using density functional theory. We introduce a solute strain misfit tensor that quantifies how solutes change lattice parameters due to the stress they induce in the host crystal. Solutes modify the elastic stiffness coefficients through volumetric changes and by altering chemical bonds. We compute each of these contributions to the elastic stiffness coefficients separately, and verify that their sum agrees with changes in the elastic stiffness coefficients computed directly using fully optimized supercells containing solutes. Computing the two elastic stiffness contributions separately is more computationally efficient and provides more information on solute effects than the direct calculations. We compute the solute dependence of polycrystalline averaged shear and Young's moduli from the solute dependence of the single-crystal C_{ij}. We apply this methodology to substitutional Al, B, Cu, Mn, Si solutes and octahedral interstitial C and N solutes in bcc Fe. Comparison with experimental data indicates that our approach accurately predicts solute-induced changes in the lattice parameter and elastic coefficients. The computed data can be used to quantify solute-induced changes in mechanical properties such as strength and ductility, and can be incorporated into mesoscale models to improve their predictive capabilities.

1. Introduction

Solutes strongly influence the structural and mechanical properties of steel alloys [1,2], and steel chemistries are tuned to balance strength, hardness, toughness, and ductility for diverse applications. Small additions of solutes modify structural parameters [3–5], elastic stiffness coefficients C_{ij} [6–9], stacking fault energies [10,11], dislocation cores [12], and phase stability [13–15], leading to alloys with properties tailored to meet increasingly stringent design requirements. At the macroscopic scale, little is known about the effect of solute chemistries on elastic properties of steels, such as Young's modulus, which is an important parameter for simulating springback in metal forming [16–18]. Accurate data on solute-induced changes in the mechanical response of bcc Fe is therefore essential for designing new ferritic steels and multiphase steels containing ferrite. However, modeling the complex interplay between the host crystal, solutes, microstructure, and other defects requires a multiscale approach with information

from smaller length-scale simulations informing mesoscale models. Density functional theory (DFT) calculations provide accurate information on solute effects in metals, and have determined solute-dislocation interactions [12,19], solute size misfits [19], and solute-dependent elastic stiffness coefficients [8,20–26]. Changes in lattice parameters and elastic stiffness coefficients can directly estimate solid-solution strengthening parameters [3,19,27,28] and changes in ductility [29]. Mesoscale phase-field [30] and crystal plasticity models [31] of multi-phase steels are sensitive to the input lattice parameters and elastic stiffness coefficients of the different phases, and DFT data on the solute-dependence of these properties can enhance the predictive capabilities of these models in lieu of experimental data [32].

In the present article, we consider the effects of the substitutional solutes Al, B, Cu, Mn, and Si, and the interstitial solutes C, and N on the lattice parameter and elastic stiffness coefficients of bcc Fe. Available experimental data indicates how these solutes influence the ferrite phase [1,2,33]. Aluminum is a deoxidizer that causes moderate age hardening by forming AlN precipitates in high-N steels. Silicon is a deoxidizer with strong solid solution strengthening and moderate age hardening, and also inhibits the formation of martensite. Boron is primarily added to increase

hardenability. Copper and Mn increase strength, and improve hardenability and toughness through grain refinement. Carbon is important in all steels since it is a highly effective hardener and strengthener, and forms carbides with other solutes. Nitrogen also increases strength by forming nitride precipitates with other solutes. Several experimental [3,4,6,28] and theoretical [7,8,22–24,26] studies determined the effects of different solutes, including Al, B, Si, Mn, C, and N, on structural and mechanical properties of bcc Fe. However, no comprehensive experiments or *ab initio* calculations have quantified the strain and chemical effects of Al, B, Cu, Mn, Si, C, and N on the lattice parameter and single-crystal elastic stiffness coefficients of bcc Fe. The lack of information on solute effects is a barrier to the broader development of crystal plasticity models of single- and multi-phase steels.

We apply DFT to compute the dependence of the bcc Fe lattice parameter and elastic stiffness coefficients on the concentration of Al, B, Cu, Mn, Si, C, and N solutes. We generalize the definition of solute size misfits [27] that quantify solute-induced volumetric expansion to more general solute-induced strains that can change the size and shape of a crystal. Solutes modify elastic stiffness coefficients through changes in crystal volume and chemical bonding [6,7,34]. Psiachos et al. [7] calculate the total and volumetric changes in the elastic stiffness coefficients of bcc Fe due to H solutes, and estimate the chemical contribution as the difference between the total and volumetric changes. We extend this approach by separately calculating the volumetric and chemical contributions to changes in the elastic stiffness coefficients. We show that the sum of these two contributions agrees with direct calculations of changes in the elastic stiffness coefficients that encompass both effects, verifying that the volumetric and chemical contributions are the dominant factors that determine how solutes modify elasticity and ultimately mechanical properties influenced by elastic response. The separate calculations of the volumetric and chemical contributions are more computationally efficient than the direct calculations, and also reveal the relative importance of solute-induced lattice strain and bonding effects for each solute.

The remainder of this paper is organized as follows. Section 2 discusses our methodology for computing solute effects on lattice parameters and elastic stiffness coefficients. We give the details of our DFT calculations for solutes in bcc Fe, and discuss the importance of choosing proper *k*-point meshes to ensure fast convergence of sensitive elastic stiffness coefficient derivatives used to determine the volumetric contributions to solute-induced changes in the elastic stiffness coefficients. The computed data and an assessment of its accuracy through comparisons with available DFT calculations and experimental data are discussed in Section 3. The major novel results in the paper are summarized in Section 4.

2. Methods

We use DFT to compute the effects of the solutes Al, B, Cu, Si, Mn, C, and N on the lattice parameter and elastic stiffness coefficients C_{ij} of bcc Fe at 0 K. Experimental measurements show that the effects of solutes and temperature on the lattice parameter [35] and elastic response [3] of bcc Fe are nearly independent. Our computed solute data can therefore be used in conjunction with separate data on temperature effects to give changes in these quantities as a function of solute concentration and temperature. We also demonstrate that the volumetric and chemical effects from solutes on the C_{ij} can be computed independently, and that their sum agrees with solute-induced changes calculated directly using cubic supercells containing a solute with the lattice parameter relaxed to give zero hydrostatic stress. It is well known that Al, Cu, Mn, and Si are substitutional solutes, and C and N are octahedral interstitial solutes in bcc Fe [2]. We treat B as a substitutional

solute since experimental measurements [36,37] supported by recent DFT calculations [8,38,39] show that at low temperature, B is more stable substitutionally than interstitially in bcc Fe. Experimental data [3] shows that the variation of the lattice parameter and polycrystalline elastic moduli of bcc Fe with solute concentration is approximately linear to ~10 at.% for a large number of solutes. Solute concentrations relevant for advanced high strength steels [40] are generally below this level, so we expand the lattice parameter and C_{ij} to first order in solute concentration and calculate the coefficients in the expansions. The similarity between the coefficients computed using $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells verifies that higher-order contributions are small in the DFT calculations for the concentration range relevant for many technologically important steels. A similar methodology can be applied to steels with larger solute concentrations, but it may be necessary to include higher-order derivatives that capture the effects of solute-solute interactions. It may also be necessary to use supercells that better represent the atomic ordering of the alloy, e.g., special quasirandom structures [41,42] can be used to model concentrated random alloys.

2.1. Effect of solutes on the lattice parameter

We define a strain misfit tensor ϵ_{ij}^s to quantify lattice distortions induced by a solute *s* as the derivative of strain e_{ij} with respect to solute concentration c_s in the dilute limit. Physically, solutes induce stress σ_{kl} in the host crystal causing the lattice to strain until the stress becomes zero. However, for computational efficiency we fix the lattice vectors of the simulation cells and compute the solute-induced strain in the linear elastic limit from the induced stress and the elastic compliance tensor S_{ijkl} as $e_{ij} = \sum_{k,l} S_{ijkl}\sigma_{kl}$. We introduce a single solute into a supercell and use DFT to compute σ_{kl} after relaxing all of the ionic positions. We approximate ϵ_{ij}^s from the number of lattice sites N in the supercell, the elastic compliance tensor S_{ijkl}^0 of the pure crystal, and the computed stress σ_{kl} as

$$\epsilon_{ij}^s = \left.\frac{\partial e_{ij}}{\partial c_s}\right|_{c_s=0} \approx N\sum_{k,l} S_{ijkl}^0 \sigma_{kl}. \tag{1}$$

The expression on the right is a finite difference approximation for the derivative, where the factor of N arises from $c_s = 1/N$. The strain misfit tensor can be computed for any crystal structure, and captures the effects of general solute-induced elastic stresses that can arise from multiple solutes in a computational supercell. Here we focus on individual substitutional and octahedral interstitial solutes in bcc Fe which do not induce shear stress.

Substitutional solutes maintain the cubic symmetry of the bcc lattice, whereas octahedral interstitial solutes induce tetragonal stress that will break cubic symmetry if the lattice is allowed to fully relax. This leads to different expressions for the strain misfit tensors. Substitutional solutes induce isotropic stress $\sigma_{ij} = \sigma_{11}\delta_{ij}$ in bcc Fe, and the resulting solute strain misfit tensor is

$$\epsilon_{ij}^s = \left.\frac{1}{a_0}\frac{\partial a}{\partial c_s}\right|_{c_s=0} \delta_{ij} \approx N(S_{1111}^0 + 2S_{1122}^0)\sigma_{11}\delta_{ij}, \tag{2}$$

where a_0 is the lattice parameter of pure Fe and δ_{ij} is the Kronecker delta. The tetragonal stress induced by octahedral interstitial solutes in bcc Fe will change the lattice parameter along one crystal axis differently than along the other two perpendicular crystal axes if the lattice is fully relaxed. The resulting body-centered tetragonal (bct) structure would have lattice parameter a_1 along two crystal axes and a different lattice parameter a_3 along the third crystal axis. A [0 0 1]-oriented octahedral interstitial solute induces stress