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.

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1. Introduction

Solute 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, 4, 5], elastic stiffness coefficients C_{ij} [6, 7, 8, 9], stacking fault energies [10, 11], dislocation cores [12], and phase stability [13, 14, 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, 17, 18]. Accurate data on solute-induced changes in the mechanical response of bcc Fe is therefore essential for designing new ferritic steels and multi-phase steels containing ferrite. However, modelling 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 [19, 12], solute size misfits [19], and solute-dependent elastic stiffness coefficients [20, 21, 22, 8]. Changes in lattice parameters and elastic stiffness coefficients can directly estimate solid-solution strengthening parameters [23, 24, 3, 19] and changes in ductility [25]. Mesoscale phase-field [26] and crystal plasticity models [27] 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 [28].

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 pa-

parameter and elastic stiffness coefficients of bcc Fe. Available experimental data indicates how these solutes influence the ferrite phase [1, 2, 29]. Aluminum is
30 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.
35 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. Experimental studies [6, 3, 24, 4] measured the effects of several solutes including Al, Si, Mn, C, and N on the structural and mechanical properties of bcc Fe, and theoretical
40 calculations determined the effects of H [7] and B [8] on the elastic stiffness coefficients. However, no comprehensive experiments or *ab initio* calculations have quantified the 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 this information is a barrier to the broader development of crystal plasticity models
45 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 [23] that quantify solute-induced volumetric expansion to more general solute-induced strains
50 that can change the size and shape of a crystal. Solutes modify elastic stiffness coefficients through changes in crystal volume and chemical bonding [6, 30, 7]. 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
55 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
60 modify elasticity and ultimately mechanical properties influenced by elastic re-
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.

65 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
70 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.

75 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 effects of solutes and temperature on the
lattice parameter [31] and elastic response [3] of bcc Fe are nearly independent.
80 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 volumet-
ric and chemical effects on the C_{ij} can be computed independently, and that
their sum agrees with solute-induced changes calculated directly using cubic
85 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 [32, 33] supported by recent DFT calculations [34, 35, 8] 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 [36] 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[37, 38] 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

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

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

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

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 [001]-oriented octahedral interstitial solute induces stress $\sigma_{ij} = \sigma_{11} \delta_{ij} (\delta_{i1} + \delta_{i2}) + \sigma_{33} \delta_{ij} \delta_{i3}$, and the resulting solute strain misfit tensor is

$$\begin{aligned} \epsilon_{ij}^s \approx & N[(S_{1111}^0 + S_{1122}^0) \sigma_{11} + S_{1122}^0 \sigma_{33}] \delta_{ij} (\delta_{i1} + \delta_{i2}) \\ & + N(2S_{1122}^0 \sigma_{11} + S_{1111}^0 \sigma_{33}) \delta_{ij} \delta_{i3}. \end{aligned} \quad (3)$$

In this case, $\epsilon_{11}^s = \epsilon_{22}^s = (1/a_0)(\partial a_1 / \partial c_s)_{c_s=0}$ and $\epsilon_{33}^s = (1/a_0)(\partial a_3 / \partial c_s)_{c_s=0}$. The strain misfit tensors for octahedral interstitial solutes in the [100]- and [010]-

orientations are obtained by appropriate permutations of the tensor indices. Our computational supercells contain a single interstitial solute with a specific
140 orientation that will transform the bcc lattice to a particular bct variant if the structure is allowed to fully relax. However, this study focuses on solute effects on the bcc ferrite phase of steels that contains many interstitials in each possible orientation causing isotropic expansion. We model this by constraining the supercells to be cubic, and determine isotropic changes in the lattice parameter
145 from average cubic strain misfits $\bar{\epsilon}^s = (\epsilon_{11}^s + \epsilon_{22}^s + \epsilon_{33}^s)/3$. The average strain misfit for substitutional solutes equals the diagonal tensor components $\bar{\epsilon}^s = \epsilon_{ii}^s$. The lattice parameter depends linearly on solute concentrations c_s in the dilute limit with linear coefficients $a_0\bar{\epsilon}^s$:

$$a(\{c_s\}) \approx a_0 + \sum_s \left. \frac{\partial a}{\partial c_s} \right|_{c_s=0} c_s = a_0 \left[1 + \sum_s \bar{\epsilon}^s c_s \right]. \quad (4)$$

2.2. Effects of solutes on the elastic stiffness coefficients

150 We determine changes in the second-order elastic stiffness coefficients $C_{\alpha\beta\gamma\delta}$ due to solute-induced strain and changes in chemical bonding through separate calculations. In the rest of the discussion we use contracted Voigt notation [39] for the elastic stiffness coefficients, where the index pairs $\alpha\beta$ and $\gamma\delta$ are replaced by single indices i and j : $C_{\alpha\beta\gamma\delta} \rightarrow C_{ij}$. We define the volumetric effect on C_{ij}
155 as the product of the pure Fe C_{ij} derivative with respect to lattice parameter a and the derivative of a with respect to solute concentration c_s determined by $\bar{\epsilon}^s$:

$$\left(\frac{\partial C_{ij}}{\partial c_s} \right)_{\text{vol}} = \left. \frac{\partial C_{ij}^0}{\partial a} \right|_{a=a_0} \cdot \left. \frac{\partial a}{\partial c_s} \right|_{c_s=0} \approx \left. \frac{\partial C_{ij}^0}{\partial a} \right|_{a=a_0} \cdot a_0 \bar{\epsilon}^s, \quad (5)$$

where C_{ij}^0 are the elastic stiffness coefficients of pure Fe. We define the chemical effect on C_{ij} as the derivative of C_{ij} with respect to c_s with a constrained to
160 equal the pure Fe lattice parameter a_0 :

$$\left(\frac{\partial C_{ij}}{\partial c_s} \right)_{\text{chem}} = \left. \frac{\partial C_{ij}^s}{\partial c_s} \right|_{\substack{a=a_0 \\ c_s=0}}, \quad (6)$$

where C_{ij}^s are the elastic stiffness coefficients of Fe containing a solute. The total derivative of an elastic stiffness coefficient $(\partial C_{ij}/\partial c_s)_{\text{tot}}$ is the sum of the volumetric and chemical contributions,

$$\left(\frac{\partial C_{ij}}{\partial c_s}\right)_{\text{tot}} = \left(\frac{\partial C_{ij}}{\partial c_s}\right)_{\text{vol}} + \left(\frac{\partial C_{ij}}{\partial c_s}\right)_{\text{chem}}. \quad (7)$$

The C_{ij} depend linearly on solute concentrations in the dilute limit,

$$C_{ij}(\{c_s\}) \approx C_{ij}^0 + \sum_s \left(\frac{\partial C_{ij}}{\partial c_s}\right)_{\text{tot}} c_s. \quad (8)$$

165 The stress in the supercells is non-zero when we compute both the chemical and the volumetric effects, and we calculate the C_{ij} in each case using stress-strain calculations rather than applying stress corrections to energy-strain calculations [40, 41, 42].

We also compute the C_{ij} derivatives directly as

$$\left(\frac{\partial C_{ij}}{\partial c_s}\right)_{\text{dir}} = \left.\frac{\partial C_{ij}^s}{\partial c_s}\right|_{a=a_{\text{eq}}, c_s=0}, \quad (9)$$

170 where a_{eq} is the equilibrium zero-pressure lattice parameter for a cubic supercell containing a single solute. The direct calculations in Eqn. 9 validate the accuracy of Eqn. 7 since the direct supercells contain a solute and have relaxed lattice parameters, thereby including both the volumetric and chemical effects. However, computing the separate volumetric and chemical terms in Eqn. 7 is 175 computationally more efficient since the C_{ij}^0 derivatives with respect to lattice parameter in the volumetric term are computed using one-atom primitive cells, and only atomic relaxations are required for computing the chemical terms. Furthermore, the separate calculations reveal the relative importance of the two different contributions in changing the anisotropic elastic response of the crystal 180 lattice.

The tetragonal stress induced by octahedral interstitial solutes breaks the cubic symmetry of the C_{ij} tensor even though the supercells are constrained to be cubic. We therefore average appropriate tensor elements [7] to obtain effective

cubic C_{ij} for bcc Fe containing C or N. For example, a [001]-oriented interstitial
 185 results in $C_{11} = C_{22} \neq C_{33}$, $C_{13} = C_{23} \neq C_{12}$, and $C_{44} = C_{55} \neq C_{66}$. The
 average cubic C_{ij} computed from the C_{ij} of bcc Fe containing a [001]-oriented
 octahedral interstitial are therefore $\overline{C_{11}} = (2C_{11} + C_{33})/3$, $\overline{C_{12}} = (C_{12} + 2C_{13})/3$,
 and $\overline{C_{44}} = (2C_{44} + C_{66})/3$. We apply seven independent strains to compute the
 six independent elastic stiffness coefficients following the least-squares fitting
 190 procedure of Trinkle [43]. Substitutional solutes induce isotropic stress which
 preserves the cubic symmetry of the elastic stiffness tensor, so no averaging is
 needed for these cases.

2.3. DFT calculation details

We use the plane-wave basis DFT code VASP [44] to compute ϵ_{ij}^s and solute-
 195 induced changes in the C_{ij} for bcc Fe. We compute the C_{ij} from stress versus
 strain after relaxing all of the ion positions in the supercells. The Perdew-Burke-
 Ernzerhof (PBE) generalized gradient approximation (GGA) functional [45] ac-
 counts for electron exchange and correlation energy, and a projector augmented
 wave (PAW) potential [46] with electronic configuration [Ar] $3d^7 4s^1$ generated by
 200 Kresse and Joubert [47] models the Fe nuclei and core electrons. The solutes Al,
 B, Cu, Mn, Si, C, and N are modelled using PAW potentials [47] with respec-
 tive electronic configurations [Ne] $3s^2 3p^1$, [He] $2s^2 2p^1$, [Ar] $3d^{10} 4s^1$, [Kr] $3d^6 4s^1$,
 [Ne] $3s^2 3p^2$, [He] $2s^2 2p^2$, and [He] $2s^2 2p^3$. The calculations require a plane-wave
 energy cutoff of 550 eV to converge the energies to less than 1 meV/atom. A
 205 conjugate gradient method relaxes the atoms until all of the atomic forces are
 less than 5 meV/Å. The energy tolerance for the electronic self-consistency loop
 is 10^{-8} eV. All of the calculations are spin polarized to model the ferromag-
 netism of bcc Fe.

Figure 1 shows that the derivatives of the pure Fe bulk modulus B_0 , shear
 210 modulus C'_0 , and C_{ij}^0 with respect to lattice parameter depend more strongly on
 k -point sampling than the energy per atom, lattice parameter a_0 , B_0 , C'_0 , and
 C_{ij}^0 . The data in the plots is generated using the one-atom bcc primitive cell. We
 compute all the properties in the figure using standard $N_k \times N_k \times N_k$ Monkhorst-

Pack (M-P) [48] k -point meshes, which are shifted off of the Γ -point for even
 215 numbers of mesh divisions. We also compute these properties using even M-P
 meshes that include the Γ -point. The energy per atom and lattice parameter
 oscillate around their converged values using Γ -centered and shifted meshes,
 but the magnitudes of the fluctuations are less than 1 meV and 1 mÅ. The
 fluctuations in the elastic moduli are relatively larger than the energy and lattice
 220 parameter fluctuations, but the values differ from the converged values by less
 than 2%. In contrast, the fluctuations in the derivatives of B_0 , C'_0 , and C_{ij}^0 with
 respect to lattice parameter are as large as 18%. These derivatives are critically
 important since they determine $(\partial C_{ij}/\partial c_s)_{\text{vol}}$ in Eqn. 5, so the standard M-P
 meshes lead to large errors in this quantity unless very dense meshes are used.
 225 An improved k -point sampling method for the bcc lattice based on the simple
 cubic lattice [49] leads to faster convergence for all of these properties. The
 individual Monkhorst-Pack meshes form fcc meshes in reciprocal space, which
 combine to form a denser simple cubic mesh (black points in Fig. 1). The values
 we report for pure Fe properties are computed using the simple cubic k -point
 230 mesh generated by combining the $34 \times 34 \times 34$ Γ -centered and shifted meshes.
 Sampling the Brillouin zone with this simple cubic mesh is also equivalent to
 averaging the results from the two separate Monkhorst-Pack calculations since
 Brillouin zone integrations are approximated as weighted sums over the k -points.
 Our $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$ cubic supercell calculations are converged
 235 to a similar level of accuracy using k -point meshes generated by combining
 $12 \times 12 \times 12$, $8 \times 8 \times 8$, and $6 \times 6 \times 6$ Γ -point-centered and shifted Monkhorst-
 Pack meshes.

The data in Figure 1 is computed using order-one Methfessel-Paxton smear-
 ing [50] to ensure accurate forces and stresses for structural relaxations and
 240 elastic stiffness coefficient calculations. We choose a smearing energy width of
 0.2 eV for our chosen k -point meshes to ensure close agreement between the
 electronic density of states (DOS) near the Fermi energy computed using the
 smearing method with the DOS computed using the linear tetrahedron method
 with Blöchl corrections [51]. We also investigated the sensitivity of the elastic

245 stiffness coefficients and their derivatives to the smearing energy width. Varying
 the smearing width from 0.15 eV to 0.25 eV causes the elastic stiffness coeffi-
 cients to change by less than $\sim 2\%$. The elastic stiffness coefficients derivatives
 are more sensitive, varying from $\sim 2\%$ for $\partial C_{12}/\partial a$ to $\sim 8\%$ for $\partial C_{44}/\partial a$. Even
 though these errors are larger, the resulting variations in the solute-induced
 250 changes in the elastic stiffness coefficients as the smearing width changes from
 0.15 eV to 0.25 eV are small. For example, the largest volumetric contributions
 are due to C and N since they induce the largest lattice strains. The changes
 in the elastic stiffness coefficients due to C and N in the $3 \times 3 \times 3$ supercell
 vary from -23.4 GPa to -22.8 GPa for C_{11} , from -14.3 GPa to -14.0 GPa for
 255 C_{12} , and from -10.3 GPa to -9.8 GPa for C_{44} . The variations for all the other
 solutes in the $3 \times 3 \times 3$ supercells, and all the solutes in the $4 \times 4 \times 4$ supercells
 are even smaller. We do not report values for the variations for the $2 \times 2 \times 2$
 supercells since these calculations generally exhibit strong finite size effects.

2.4. Computational workflow

260 Figure 2 summarizes the workflow for computing ϵ_{ij}^s and the C_{ij} derivatives
 with respect to c_s . The process begins with calculating a_0 , C_{ij}^0 , and the C_{ij}^0
 derivatives with respect to lattice parameter for pure Fe. The ϵ_{ij}^s calculations
 follow, which require the pure Fe lattice parameter a_0 and elastic stiffness coeffi-
 cients C_{ij}^0 as inputs. The final sets of calculations determine the C_{ij} derivatives
 265 with respect to c_s . These calculations require inputs from the pure Fe and solute
 strain misfit calculations.

We start with optimizing the lattice parameter a_0 of pure Fe by computing
 the cell pressure for a small range of lattice parameter values centered around the
 experimental value. We then perform a quadratic fit to this data and determine
 270 the lattice parameter value where the fitted pressure is zero. The DFT-computed
 pressure for the optimal lattice parameter $a_0 = 2.832$ Å is less than 0.001 GPa.
 This lattice parameter is an input for computing the C_{ij}^0 of pure Fe, the solute
 strain misfits in Eqns. 2 and 3, and the volumetric and chemical contributions
 to the C_{ij} derivatives with respect to solute concentration in Eqns 5 and 6,

275 respectively.

The next set of calculations determine the single-crystal C_{ij}^0 of pure bcc Fe, which relate stress σ_i to strain e_j in the linear elastic limit as $\sigma_i = \sum_j C_{ij}^0 e_j$. The computational cells in this set of calculations have the a_0 value computed in the previous step. We apply volumetric strains to compute the bulk modulus
280 $B_0 = (C_{11}^0 + 2C_{12}^0)/3$, volume-conserving orthorhombic strains [52] to compute the shear modulus $C'_0 = (C_{11}^0 - C_{12}^0)/2$, and volume-conserving monoclinic strains [52] to compute the shear modulus C_{44}^0 . We use strain values of $\pm 0.25\%$ and $\pm 0.5\%$, which produce a linear stress-strain relation in each case. The slopes of the resulting stress-strain curves computed using a four-point central
285 finite difference [53] give B_0 , C'_0 , and C_{44}^0 , and we solve for C_{11}^0 and C_{12}^0 from B_0 and C'_0 . The computed values are $C_{11}^0 = 278$ GPa, $C_{12}^0 = 148$ GPa, and $C_{44}^0 = 98$ GPa. We determine the C_{ij}^0 derivatives with respect to lattice parameter by computing C_{11}^0 , C_{12}^0 , and C_{44}^0 for the lattice parameter values $a_0 \pm 0.005$ Å and $a_0 \pm 0.01$ Å. We use the same four-point central difference formula to
290 calculate the derivatives. The computed values are $(\partial C_{11}^0 / \partial a)|_{a \rightarrow a_0}^{c_s=0} = -1323$ GPa/Å, $(\partial C_{12}^0 / \partial a)|_{a \rightarrow a_0}^{c_s=0} = -828$ GPa/Å, and $(\partial C_{44}^0 / \partial a)|_{a \rightarrow a_0}^{c_s=0} = -576$ GPa/Å. The C_{ij}^0 are inputs for the solute strain misfit calculations in Eqns. 2 and 3, the chemical contributions to the C_{ij} derivatives with respect to solute concentration in Eqn. 6, and the direct calculations of these C_{ij} derivatives in Eqn. 9
295 (see Fig. 2). The C_{ij}^0 derivatives with respect to lattice parameter are inputs for the volumetric contributions to the C_{ij} derivatives with respect to solute concentration in Eqn. 5.

The solute strain misfit calculations follow next, which use $2 \times 2 \times 2$ (16 lattice sites), $3 \times 3 \times 3$ (54 lattice sites), and $4 \times 4 \times 4$ (128 lattice sites) cubic
300 supercells with the pure Fe lattice parameter a_0 containing a single substitutional or octahedral interstitial solute atom. We constrain the supercell lattice vectors and relax the ionic positions. The stress σ_{kl} in the supercells is non-zero after relaxing the atoms due to the constraint we impose on the lattice vectors. The number of lattice sites N , the stress σ_{kl} , and the elastic compliance coefficients S_{ijkl}^0 computed from the C_{ij}^0 determine the solute strain misfit tensors,
305

using Eqn. 2 for substitutional solutes and Eqn.3 for interstitial solutes. The average $\overline{\epsilon^s}$ of the diagonal tensor values ϵ_{ii}^s for each solute is an input for calculating the volumetric contributions to the C_{ij} derivatives with respect to solute concentration in Eqn. 5. The $\overline{\epsilon^s}$ values also provide initial estimates for the
 310 zero-pressure lattice parameter for each supercell with a solute. These initial lattice parameters and the atomic positions in the supercells are then optimized to give zero-pressure. The final geometries are strained to directly calculate the C_{ij} derivatives with respect to solute concentration.

The chemical and volumetric contributions to the C_{ij} derivatives with re-
 315 spect to solute concentration both require inputs from the calculations discussed above, but are independent of each other. We approximate the chemical contributions in Eqn. 6 using finite differences as

$$\left(\frac{\partial C_{ij}}{\partial c_s}\right)_{\text{chem}} \approx N[C_{ij}^s(a_0) - C_{ij}^0], \quad (10)$$

where $C_{ij}^s(a_0)$ are elastic stiffness coefficients computed using cubic $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$ supercells with the pure Fe lattice parameter a_0 that contain
 320 a single solute. We compute $C_{ij}^s(a_0)$ by applying the three independent strains used in the pure Fe calculations to the supercells containing substitutional solutes, and the seven independent strains discussed in the Methods section to the supercells containing interstitial solutes. The atoms are relaxed after applying strain in each case, and the elastic stiffness coefficients are extracted from the
 325 slopes of the DFT-computed stresses versus the applied strains. The volumetric contributions for each solute are computed from the pure Fe C_{ij}^0 derivatives with respect to lattice parameter, the pure Fe lattice parameter a_0 , and the average solute strain misfit $\overline{\epsilon^s}$ using Eqn. 5. The C_{ij} derivatives from the chemical and volumetric calculations are input for the total contribution calculations in
 330 Eqn. 7 which sum these two independent contributions.

The final set of DFT calculations in Fig. 2 labeled “Direct calculations” compute the total C_{ij} derivatives directly using cubic supercells that contain a single solute at their relaxed zero-pressure lattice parameter a_{eq} . This di-

rect method encompasses both the chemical and volumetric contributions since
 335 the supercells contain a solute and are at their equilibrium lattice parameters.
 However, the direct calculations give less information since the two mechanisms
 causing the changes in the elastic stiffness coefficients are not separated. The
 direct calculations are also more computationally expensive than the separate
 calculations since the atomic positions and the supercell volume must be simul-
 340 taneously optimized. The coupling between the lattice and atomic degrees of
 freedom, as well as the changes in the number of plane-wave basis functions
 that accompany changes in volume, can lead to a non-negligible increase in the
 total number of electronic steps required to relax the system. For example, we
 found that fully optimizing the atomic positions and supercell lattice vectors
 345 when a solute is present in a supercell can require more than twice as many
 electronic steps relative to optimizing just the atomic positions with a solute in
 the supercell. Simultaneously optimizing all degrees of freedom can therefore
 result in a large increase in total computational time, especially for large su-
 percells or high throughput studies involving many different solute chemistries.
 350 A potential advantage of the direct method is that it can capture coupling be-
 tween the volumetric and chemical effects on the elastic stiffness coefficients not
 accounted for in the sum in Eqn. 7. We validate the accuracy of computing the
 derivatives of the C_{ij} with respect to solute concentration as the sum of the
 separate chemical and volumetric terms by comparing the results to the direct
 355 calculations of these C_{ij} derivatives. We approximate the direct calculations in
 Eqn. 9 using finite differences similar to Eqn. 10:

$$\left(\frac{\partial C_{ij}}{\partial c_s}\right)_{\text{dir}} \approx N[C_{ij}^s(a_{\text{eq}}) - C_{ij}^0], \quad (11)$$

where $C_{ij}^s(a_{\text{eq}})$ is computed using cubic supercells that contain a single solute at
 their equilibrium zero-pressure lattice parameter a_{eq} . We use the same method-
 ology as the chemical contributions to compute the elastic stiffness coefficients
 360 for these direct calculations.

3. Results and Discussion

Figure 3 compares the strain misfit tensors for the substitutional and interstitial solutes and shows convergence with respect to supercell size. The strain misfit tensors are isotropic for substitutional solutes, with each diagonal element equal to the average value. The strain misfit tensors are anisotropic for
365 interstitial solutes so we show the two independent components along with the average values. The strain misfits for substitutional Al, Cu, and Mn have similar positive values for the two largest supercell sizes, showing that these solutes cause the lattice to expand by similar amounts. Boron has a larger negative
370 strain misfit reflecting its small ionic radius, which causes a larger lattice contraction. The Si strain misfit is nearly an order of magnitude smaller than the strain misfits of the other substitutional solutes, showing that Si has a smaller effect on the lattice parameter. The interstitial solutes have large positive strain misfits along the octahedral orientation direction and small negative strain misfits in the perpendicular directions, as discussed in Subsection 2.1. Note that
375 the interstitial strain misfits are at least an order of magnitude larger than the substitutional strain misfits. This is due to large stress induced in the lattice by the close separation between the interstitial atom and its nearest Fe neighbors along the octahedral orientation direction. We compare our computed Al, Mn, Si, C, and N values to experimental data in the Data Validation section.
380

The strain misfits are inputs for Eqn. 4 which gives the lattice parameter as a function of solute concentration, and also determine the volumetric contributions to the elastic stiffness coefficient derivatives with respect to solute concentration in Eqn. 5. The concentration-dependent lattice parameter can be
385 used directly as input for mesoscale models, and the solute strain misfits are generally a good indicator of the solid-solution strengthening of each solute [3]. Based on the strain misfit values, interstitial C and N should produce the largest increase in strength since they have the largest strain misfits followed by B. The solutes Al, Cu, and Mn should produce the next highest increase in strength,
390 while the low value of the Si strain misfit indicates that it should have a small

effect. The computed Si strain misfit agrees well with experimental data (see the Data Validation section), but Si is known to have a high strengthening potency in bcc Fe [24, 3] which has been attributed to strong elastic interactions between Si solutes and screw dislocations [24]. The computed values vary between the
395 three different supercells sizes, with the $2 \times 2 \times 2$ calculations subject to the largest finite size effects due to the small supercell size. The small variation between the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ values are due to competing sources of error. The solute concentration that results from the $3 \times 3 \times 3$ supercell size (1.85 at.%) is further from the dilute limit than the concentration from the $4 \times 4 \times 4$
400 supercell size (0.78 at.%), and the $3 \times 3 \times 3$ supercell results are subject to larger finite size effects than the $4 \times 4 \times 4$ supercell results. The $4 \times 4 \times 4$ supercells are closer to the dilute limit, but the effects of solutes are smaller and the results are more sensitive to numerical errors. To help offset these competing errors we perform linear fits to the lattice parameter changes due to each solute in
405 the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells, constrained to give the pure Fe lattice parameter a_0 for zero solute concentration. Table 1 lists the lattice parameter derivatives with respect to solute concentration which are slopes of the linear fits.

Figure 4 compares the volumetric and chemical contributions to the C_{ij}
410 derivatives with respect to solute concentration (Eqns. 5 and 6) and shows that sums of these terms (Eqn. 7) agree well with the direct calculations (Eqn. 9). The bars representing $(\partial C_{ij}/\partial c_s)_{\text{vol}}$ and $(\partial C_{ij}/\partial c_s)_{\text{chem}}$ are stacked on each other when these terms have the same sign so that the total length of both bars represents the sum of the two terms. If the terms have opposite signs, the larger
415 of the two bars is shifted vertically from the axis so that the bars overlap to emphasize the partial cancellation between $(\partial C_{ij}/\partial c_s)_{\text{vol}}$ and $(\partial C_{ij}/\partial c_s)_{\text{chem}}$. For example, the bars corresponding to $(\partial C_{11}/\partial c_{\text{B}})_{\text{chem}}$ for each supercell size with B (medium red, blue, and orange) have been shifted upwards out of the negative range by an amount equal to that of the volumetric contributions
420 (light red, blue, and orange) which are entirely in the positive range. The agreement between the sum of chemical and volumetric contributions with the

Table 1: Derivatives of the lattice parameter a , single-crystal C_{ij} , VRH average polycrystalline Young's modulus E_{VRH} and shear modulus G_{VRH} , and Pugh ratio $B_{\text{VRH}}/G_{\text{VRH}}$ with respect to solute concentration c_s . The values for the a and C_{ij} derivatives are the slopes of linear fits to the data from the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells. The values for the E_{VRH} , G_{VRH} , and $B_{\text{VRH}}/G_{\text{VRH}}$ derivatives are computed using Eqns. A.15–A.17 in the Appendix. The lattice parameter and C_{ij} as a function of solute concentration are $a(\{c_s\}) = a_0 + \sum_{c_s} (\partial a / \partial c_s)_{c_s=0} \cdot c_s$ and $C_{ij}(\{c_s\}) = C_{ij}^0 + \sum_{c_s} (\partial C_{ij} / \partial c_s)_{\text{tot}} \cdot c_s$. Similar expressions give the solute dependence of E_{VRH} , G_{VRH} , and $B_{\text{VRH}}/G_{\text{VRH}}$. The lattice parameter derivatives have units of mÅ/at.% and the C_{ij} , E_{VRH} , and G_{VRH} derivatives have units of GPa/at.%. The $B_{\text{VRH}}/G_{\text{VRH}}$ derivatives have units of 1/at.%.

Solute s	Al	B	Cu	Mn	Si	C	N
$\left. \frac{\partial a}{\partial c_s} \right _{c_s=0}$	1.66	−2.96	1.86	2.04	−0.29	8.97	9.27
$\left(\frac{\partial C_{11}}{\partial c_s} \right)_{\text{tot}}$	−12.62	−10.98	−11.06	−8.40	−9.55	−5.18	−5.93
$\left(\frac{\partial C_{12}}{\partial c_s} \right)_{\text{tot}}$	−7.10	−4.21	−3.95	−5.26	−4.77	−2.66	−3.95
$\left(\frac{\partial C_{44}}{\partial c_s} \right)_{\text{tot}}$	1.18	−1.33	−1.52	0.57	2.04	−2.56	−2.32
$\left. \frac{\partial E_{\text{VRH}}}{\partial c_s} \right _{c_s=0}$	−3.18	−6.47	−6.86	−2.10	−1.37	−4.96	−4.52
$\left. \frac{\partial G_{\text{VRH}}}{\partial c_s} \right _{c_s=0}$	−0.83	−2.42	−2.60	−0.52	−0.20	−1.95	−1.68
$\left. \frac{\partial}{\partial c_s} \left(\frac{B_{\text{VRH}}}{G_{\text{VRH}}} \right) \right _{c_s=0}$	−0.085	−0.011	−0.004	−0.062	−0.071	0.012	−0.009

direct calculations verifies that the separation of the chemical and volumetric contributions accounts for all of the essential physics that determines how solutes change the elasticity of bcc Fe. The chemical contributions are negative for
 425 most of the substitutional solutes, and larger than the volumetric contributions in most of the cases. All of the substitutional solutes cause C_{11} and C_{12} to decrease, which shows that these solutes cause a local weakening of bonds around the solute atom. Boron and Cu cause C_{44} to decrease, whereas Al, Mn, and Si cause C_{44} to increase. The interstitial solutes have large positive chemical
 430 contributions to the three C_{ij} derivatives, since the interstitial atoms stiffen bonds by pushing neighboring Fe atoms closer together than in bulk. The large negative volumetric contributions of the interstitials reflects their large strain misfits. The two contributions partially cancel resulting in total values with magnitudes smaller or similar to the substitutional solute values for C_{11} and C_{12}
 435 derivatives, and larger for the C_{44} derivatives. Interstitial C and N cause all the C_{ij} to decrease with increasing solute concentration. The solute-dependent C_{ij} determined by $(\partial C_{ij}/\partial c_s)_{\text{tot}}$ can be used directly as input for mesoscale models, and to predict solute-induced changes in the polycrystalline elastic moduli and Pugh ratio to estimate the influence of the solutes on ductility. Similar to the
 440 lattice parameter case, we perform linear fits to the total C_{ij} data from the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercell calculations to help offset competing finite-size and numerical errors. Table 1 lists the C_{ij} derivatives with respect to solute concentration which are the slopes of the linear fits.

Table 1 lists the derivatives of the Voigt-Reuss-Hill (VRH) average polycrys-
 445 talline Young's modulus E_{VRH} , shear modulus G_{VRH} , and Pugh ratio $B_{\text{VRH}}/G_{\text{VRH}}$ with respect to solute concentration, where B_{VRH} is the VRH bulk modulus. The derivatives are computed using Eqns. A.15–A.17 in the Appendix, which require the single-crystal $\partial C_{ij}/\partial c_s$, bulk modulus $B = (C_{11} + 2C_{12})/3$, shear modulus $C' = (C_{11} - C_{12})/2$, and C_{44} as input. The dilute-limit values listed
 450 in the table are computed using the fitted $(\partial C_{ij}/\partial c_s)_{\text{tot}}$ values in the table and the pure Fe bulk modulus B_0 , shear modulus $C'_0 = (C_{11}^0 - C_{12}^0)/2$, and C_{44}^0 . All of the solutes cause E and G to decrease, with Cu and B having the largest

effect, followed by C and N, and then Al, Mn, and Si. The solutes Cu, B, C, and N cause the smallest changes in the Pugh ratio, indicating that they have the smallest influence on ductility. The solutes Al, Mn, and Si lead to the largest decreases in the Pugh ratio, and corresponding decreases in ductility. We compare the computed dependence of E_{VRH} and G_{VRH} on Mn and C concentration to experimentally measured data in the Data Validation section.

3.1. Data Validation

We evaluate the accuracy of our computed pure Fe properties by comparing the results to previous plane-wave GGA DFT calculations [54, 55, 56, 57, 8] and available experimental data [58, 59, 60]. Our lattice parameter value $a_0 = 2.832$ Å closely matches the previous GGA results of 2.84-2.85 Å, and agrees well with the experimental value of 2.866 Å measured at 4.2 K. Our elastic stiffness coefficient values $C_{11}^0 = 278$ GPa, $C_{12}^0 = 148$ GPa, and $C_{44}^0 = 98$ GPa are similar to the previous GGA results of $C_{11}^0 = 249$ -291 GPa, $C_{12}^0 = 139$ -151 GPa, and $C_{44}^0 = 70$ -110 GPa and the experimental values $C_{11}^0 = 243.1$ GPa, $C_{12}^0 = 138.1$ GPa, and $C_{44}^0 = 121.9$ GPa measured at 4.2 K. We convert our C_{ij}^0 derivatives with respect to lattice parameter into derivatives with respect to pressure for direct comparison with experimental data measured at 300 K. The conversion factor is $-3B_0/a_0$, where B_0 is the bulk modulus. Our computed values $\partial C_{11}^0/\partial P = 6.54$, $\partial C_{12}^0/\partial P = 4.09$, and $\partial C_{44}^0/\partial P = 2.85$ closely match two sets of experimental values: $\partial C_{11}^0/\partial P = 7.52, 6.72$, $\partial C_{12}^0/\partial P = 5.20, 4.58$, and $\partial C_{44}^0/\partial P = 2.66, 2.59$. The good agreement of our calculations with experiment shows that plane-wave GGA calculations accurately model the structural and elastic properties of bcc Fe.

We evaluate the accuracy of the computed strain misfits by comparing the corresponding predicted lattice parameters to the lattice parameters of cubic supercells containing the different solutes relaxed to yield zero pressure, and by direct comparison to available experimental data. The largest relative error between the predicted and directly computed lattice parameter values is 0.14% for N in the $2 \times 2 \times 2$ supercell. The errors for the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells

are less than 0.02% for all the solutes. We have also removed the constraint of cubic symmetry for the supercells with [001]-octahedral C and fully optimized the geometry to verify the accuracy of Eqn. 3. The largest error of 1.56% occurs in the [100] and [010] directions for the $2 \times 2 \times 2$ supercell. The errors in all three directions for the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells are less than 0.06%. Thus, the strain misfits accurately predict the relaxed DFT lattice parameters for all the solutes. Our computed solute strain misfits for Al of +0.056 for the $3 \times 3 \times 3$ supercell and +0.075 for the $4 \times 4 \times 4$ supercell agree well with the experimental value of +0.063 extracted from solid-solution strengthening measurements on Fe containing 5.85 at.% Al at 300 K [24]. The Si strain misfit is nearly an order of magnitude smaller than the values for the other substitutional solutes. The $3 \times 3 \times 3$ supercell value is -0.012 and the $4 \times 4 \times 4$ supercell value is +0.003. This agrees with experimental data which show Si has a small effect on the bcc Fe lattice parameter, with measured misfit values ranging from -0.0084 for 1.38 at.% Si [3] to -0.023 for 8.30 at.% Si [24]. Our computed Mn value of +0.072 is about three times larger than the experimental value of 0.0234 for 2.97 at.% Mn [3]. This may be due to inaccuracies within the DFT calculations for Mn in bcc Fe or clustering effects between Mn atoms that are absent in our supercell models, but a detailed study is needed to clarify these issues. Our average strain misfit values for C and N of +0.314 and +0.315, respectively, are larger than any of our computed substitutional solute strain misfits. This is similar to the experimental trend, where the average strain misfit values for C and N of +0.227 and +0.242 extracted from lattice parameter measurements for the bct martensite phase containing C or N [4] are larger than the measured strain misfits for substitutional Al, Mn, and Si. The differences between the experimental and computed strain misfit values cause the error in the predicted changes in lattice parameter to increase by less than 0.1% per 1% increase in solute concentration, even for Mn which shows the largest deviation from the experimental data.

The agreement between the sum of $(\partial C_{ij}/\partial c_s)_{\text{vol}}$ and $(\partial C_{ij}/\partial c_s)_{\text{chem}}$ with $(\partial C_{ij}/\partial c_s)_{\text{dir}}$ shown in Fig. 4 validates our computation approach, and com-

parison with available experimental data assesses the accuracy of the computed
515 data. To our knowledge there is no available experimental data on the solute
dependence of the single-crystal C_{ij} of bcc Fe, but the variation of the polycrys-
talline E and G with Mn and C concentration has been measured [6]. Figure 5
compares this data to the Voigt-Reuss-Hill polycrystalline averages computed
from our single-crystal data. Both Mn and C cause E and G to decrease, with
520 C having the largest effect. The similarity between the measured and computed
data shows that our calculations predict the correct trends for the effects of
Mn and C solutes on the polycrystalline moduli. The agreement between the
magnitudes of the measured and computed data is also reasonable. The main
source of error is the overestimation of the volumetric contributions to the C_{ij}
525 derivatives, which is due to the computed strain misfit values for Mn and C
being larger than the experimental values. The errors between the measured
and computed polycrystalline moduli are substantially reduced if we use the
experimental strain misfits to compute the volumetric contributions.

4. Conclusions

530 We present an efficient computational methodology to generate datasets on
how solutes change the lattice parameters and elastic stiffness coefficients of
single crystals. We provide a tensor generalization of the well-known concept
of solute size misfit to describe lattice deformations due to anisotropic solute-
induced stresses. Solute change the elastic stiffness coefficients C_{ij} through
535 volumetric and chemical effects, which are indicative of the amount of expan-
sion or contraction caused by the insertion of a solute atom into the host lattice
and changes in local chemical bonding in the lattice around the solute. We
demonstrate that these two contributions can be computed separately at an ac-
curacy comparable to more computationally expensive direct calculations. The
540 computed solute dependence of the single-crystal C_{ij} can be used to compute
the solute dependence of the polycrystalline bulk modulus B , shear modulus
 G , and Young’s modulus E using standard averaging techniques, such as the

Voigt-Reuss-Hill procedure which applies to statistically isotropic microstructures. We apply our methodology to substitutional Al, B, Cu, Mn, and Si solutes, and interstitial C and N solutes in bcc Fe, and show that the computed data agrees with available experimental data on solute effects in this phase of Fe. The computed data can be used to estimate how solutes effect mechanical properties like strength and ductility, and serve as input to increase the fidelity of larger length-scale mesoscopic models including crystal plasticity simulations. Additionally, the methods used to compute the effects of Al, B, Cu, Mn, Si, C, and N on bcc Fe can be applied to other solutes in other host lattices with different crystal symmetries. Thus, the framework presented can be applied with appropriate generalizations to computing solute effects on other Fe phases like austenite and martensite which can be incorporated into models of multiphase steels. Moreover, the methodology we present can also be used to compute changes in lattice parameters and elastic stiffness of insulating crystals due to charged point defects provided that the stress tensors are computed accurately using DFT. For charged defects, this requires properly accounting for the charge states as shown in Ref. [61] for size misfits in aliovalently doped SrTiO_3 . We provide the solute strain misfits and the single-crystal elastic stiffness coefficient derivatives with respect to solute concentration for the three different supercell sizes, along with the data for pure Fe in CSV files stored in the NIST dSpace repository (<http://hdl.handle.net/11256/671>). Reference [62] gives further information on the data stored in the repository and the format of the data files.

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585 University of Illinois.

Appendix A. Polycrystalline elastic moduli

Here we give the Voigt, Reuss, and Voigt-Reuss-Hill expressions for the bulk modulus B , shear modulus G , and Young's modulus E of an isotropic polycrystalline material, derived from the single-crystal elastic stiffness coefficients
590 C_{ij} [63]. The Voigt averages are derived under the assumption of uniform strain throughout the sample, and present an upper bound on B and G . The Reuss averages are derived under the assumption of uniform stress, and present a lower bound on B and G . The Voigt-Reuss-Hill values of these moduli are averages of the upper Voigt and lower Reuss bounds. The focus of this study is bcc Fe, so
595 we only give expression that are valid for cubic crystals. Experiments usually measure G and E , and derive B values from the relation $B = GE/(9G - 3E)$ (see, e.g, Ref. [6]). The Voigt (V) averages for the moduli are

$$B_V = \frac{C_{11} + 2C_{12}}{3}, \quad (\text{A.1})$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}, \quad (\text{A.2})$$

$$E_V = \frac{(C_{11} + 2C_{12})(C_{11} - C_{12} + 3C_{44})}{2C_{11} + 3C_{12} + C_{44}}, \quad (\text{A.3})$$

where the C_{ij} depend on solute concentration c_s . The Reuss (R) averages for the moduli are

$$B_R = \frac{C_{11} + 2C_{12}}{3}, \quad (\text{A.4})$$

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{3(C_{11} - C_{12}) + 4C_{44}}, \quad (\text{A.5})$$

$$E_R = \frac{5(C_{11} - C_{12})(C_{11} + 2C_{12})C_{44}}{C_{11}^2 - C_{12}(2C_{12} - C_{44}) + C_{11}(C_{12} + 3C_{44})}. \quad (\text{A.6})$$

600 The Voigt-Reuss-Hill (VRH) $B_{\text{VRH}} = (B_V + B_R)/2$ and $G_{\text{VRH}} = (G_V + G_R)/2$ are

$$B_{\text{VRH}} = \frac{C_{11} + 2C_{12}}{3}, \quad (\text{A.7})$$

$$G_{\text{VRH}} = \frac{3(C_{11} - C_{12})^2 + 38(C_{11} - C_{12})C_{44} + 12C_{44}^2}{30(C_{11} - C_{12}) + 40C_{44}}. \quad (\text{A.8})$$

The VRH polycrystalline Young's modulus is most simply written as

$$E_{\text{VRH}} = \frac{9B_{\text{VRH}}G_{\text{VRH}}}{3B_{\text{VRH}} + G_{\text{VRH}}}. \quad (\text{A.9})$$

We note that E_{VRH} is not equivalent to $E_{\text{avg}} = (E_V + E_R)/2$, but they have similar values and similar derivatives for the solutes we consider in this study.

605 The relative error between the dilute-limit values of the two derivatives range from 0.02% for C to 0.4% for Si.

We present the derivatives of G and E with respect to solute concentration c_s in terms of the C_{ij} derivatives with respect to c_s . The coefficients in the expressions depend on C_{11} , C_{12} and C_{44} , but the expressions are simpler when

610 written in terms of the single-crystal bulk modulus $B = (C_{11} + 2C_{12})/3$, shear
modulus $C' = (C_{11} - C_{12})/2$, and C_{44} . These derivatives evaluated at $c_s = 0$ give
the first order changes in the polycrystalline moduli with c_s . We also present the
derivative of the Pugh ratio B/G with respect to c_s within the Voigt-Reuss-Hill
approximation. The Pugh ratio estimates the ductility of a material [25, 64],
615 with values greater than ~ 1.75 indicating ductile behavior and values lower
than this indicating brittle behavior. The derivative of the Pugh ratio with
respect to c_s can be used to estimate the effect solutes have on ductility. The
derivatives of G_V and E_V with respect to c_s are

$$\frac{\partial G_V}{\partial c_s} = \frac{1}{5} \left(\frac{\partial C_{11}}{\partial c_s} - \frac{\partial C_{12}}{\partial c_s} \right) + \frac{3}{5} \frac{\partial C_{44}}{\partial c_s}, \quad (\text{A.10})$$

$$\begin{aligned} \frac{\partial E_V}{\partial c_s} = (15B + 2C' + 3C_{44})^{-2} & \left\{ \left[135B^2 + 3(2C' + 3C_{44})^2 \right] \frac{\partial C_{11}}{\partial c_s} \right. \\ & \left. - \left[135B^2 - 6(2C' + 3C_{44})^2 \right] \frac{\partial C_{12}}{\partial c_s} + 405B^2 \frac{\partial C_{44}}{\partial c_s} \right\}. \end{aligned} \quad (\text{A.11})$$

The derivatives of G_R and E_R with respect to c_s are

$$\frac{\partial G_R}{\partial c_s} = (3C' + 2C_{44})^{-2} \left[5C_{44}^2 \left(\frac{\partial C_{11}}{\partial c_s} - \frac{\partial C_{12}}{\partial c_s} \right) + 15C'^2 \frac{\partial C_{44}}{\partial c_s} \right], \quad (\text{A.12})$$

$$\begin{aligned} \frac{\partial E_R}{\partial c_s} = (9BC' + 6BC_{44} + 5C'C_{44})^{-2} & \left[15C_{44}^2 (9B^2 + 5C'^2) \frac{\partial C_{11}}{\partial c_s} \right. \\ & \left. - 15C_{44}^2 (9B^2 - 10C'^2) \frac{\partial C_{12}}{\partial c_s} + 405B^2 C'^2 \frac{\partial C_{44}}{\partial c_s} \right]. \end{aligned} \quad (\text{A.13})$$

620 The derivatives of B_{VRH} , G_{VRH} , and E_{VRH} with respect to c_s are

$$\frac{\partial B_{VRH}}{\partial c_s} = \frac{1}{3} \frac{\partial C_{11}}{\partial c_s} + \frac{2}{3} \frac{\partial C_{12}}{\partial c_s}, \quad (\text{A.14})$$

$$\frac{\partial G_{\text{VRH}}}{\partial c_s} = (3C' + 2C_{44})^{-2} \left[\frac{9C'^2 + 12C'C_{44} + 29C_{44}^2}{10} \left(\frac{\partial C_{11}}{\partial c_s} - \frac{\partial C_{12}}{\partial c_s} \right) + \frac{51C'^2 + 18C'C_{44} + 6C_{44}^2}{5} \frac{\partial C_{44}}{\partial c_s} \right], \quad (\text{A.15})$$

$$\frac{\partial E_{\text{VRH}}}{\partial c_s} = (3B_{\text{VRH}} + G_{\text{VRH}})^{-2} \left(9G_{\text{VRH}}^2 \frac{\partial B_{\text{VRH}}}{\partial c_s} + 27B_{\text{VRH}}^2 \frac{\partial G_{\text{VRH}}}{\partial c_s} \right). \quad (\text{A.16})$$

The derivative of the Pugh ratio $B_{\text{VRH}}/G_{\text{VRH}}$ with respect to c_s is

$$\frac{\partial}{\partial c_s} \left(\frac{B_{\text{VRH}}}{G_{\text{VRH}}} \right) = \frac{1}{G_{\text{VRH}}} \frac{\partial B_{\text{VRH}}}{\partial c_s} - \frac{B_{\text{VRH}}}{G_{\text{VRH}}^2} \frac{\partial G_{\text{VRH}}}{\partial c_s}. \quad (\text{A.17})$$

We give numerical values of Eqns. A.15–A.17 in Table 1 for the solutes Al, B, Cu, Mn, Si, C, and N in the dilute limit. We use the total derivative values $(\partial C_{ij}/\partial c_s)_{\text{tot}}$ in the table for $(\partial C_{ij}/\partial c_s)_{c_s=0}$ in Eqns. A.15–A.17. The single-crystal C_{ij}^0 needed to compute the coefficients in Eqns. A.15–A.17 in the dilute limit are given in Subsection 2.4.

References

- [1] W. C. Leslie, *The Physical Metallurgy of Steels*, Techbooks, Herndon, 1991.
- [2] H. Berns, W. Theisen, *Ferrous Materials: Steel and Cast Iron*, Springer-Verlag, Berlin, 2008.
- [3] W. C. Leslie, Iron and its dilute substitutional solid solutions, *Metal. Trans.* 3 (1972) 5–26.
- [4] L. Cheng, A. Böttger, T. H. de Keijser, E. J. Mittemeijer, Lattice parameters of iron-carbon and iron-nitrogen martensites and austenites, *Scripta Metal. Mater.* 24 (1990) 509–514.

- [5] C. M. Chu, H. Huang, P. W. Kao, D. Gan, Effect of alloying chemistry on the lattice constant of austenitic Fe-Mn-Al-C alloys, *Scripta Metal. Mater.* 30 (1994) 505–508.
- [6] G. R. Speich, A. J. Schwoeble, W. C. Leslie, Elastic constants of binary iron-base alloys, *Metall. Trans.* 3 (1972) 2031–2037.
- [7] D. Psiachos, T. Hammerschmidt, R. Drautz, *Ab initio* study of the modification of elastic properties of α -iron by hydrostatic strain and by hydrogen interstitials, *Acta Mater.* 59 (2011) 4255–4263.
- [8] A. F. Bialon, T. Hammerschmidt, R. Drautz, *Ab initio* study of boron in α -iron: Migration barriers and interaction with point defects, *Phys. Rev. B* 87 (2013) 104109–1–104109–13.
- [9] M. Souissi, H. Numakura, Elastic properties of FeC and FeN martensites, *ISIJ Int.* 55 (2015) 1512–1521.
- [10] A. Abbasi, A. Dick, T. Hickel, J. Neugebauer, First-principles investigation of the effect of carbon on the stacking fault energy of FeC alloys, *Acta. Mat.* 59 (2011) 3041–3048.
- [11] N. I. Medvedeva, M. S. Park, D. C. V. Aken, J. E. Medvedeva, First-principles study of Mn, Al and C distribution and their effect on stacking fault energies in fcc Fe, *J. Alloys Comp.* 582 (2014) 475–482.
- [12] L. Ventelon, B. Luthi, E. Clouet, L. Proville, B. Legrand, D. Rodney, F. Willaime, Dislocation core reconstruction induced by carbon segregation in bcc iron, *Phys. Rev. B* 91 (2015) 220102–1(R)–220102–5(R).
- [13] L. Samek, E. D. Moor, J. Penning, B. C. D. Cooman, Influence of alloying elements on the kinetics of strain-induced martensitic nucleation in low-alloy, multiphase high-strength steels, *Metal. Mater. Trans. A* 37 (2006) 109–124.

- [14] E. Sak-Saracinco, H. M. Urbassek, Free energies of austenite and martensite
fec alloys: an atomistic study, *Phil. Mag.* 94 (2013) 933–945.
- [15] X. Zhang, T. Hickel, J. Rogal, S. Fähler, R. Drautz, J. Neugebauer, Struc-
665 tural transformations among austenite, ferrite and cementite in Fe-C alloys:
A unified theory based on *ab initio* simulations, *Acta Mater.* 99 (2015) 281–
289.
- [16] B. Harris, The influence of some solutes on young’s modulus of niobium,
J. Less Common Met. 12 (1967) 247–250.
- 670 [17] W. Gan, S. S. Babu, N. Kapustka, R. H. Wagoner, Microstructural effects
on the springback of advanced high-strength steel, *Metall. Mater. Trans. A*
37 (2006) 3221–3231.
- [18] A. Andersson, Numerical and experimental evaluation of springback in ad-
vanced high strength steel, *J. Mater. Eng. Perform.* 16 (2007) 301–307.
- 675 [19] J. Yasi, L. G. H. Jr., D. R. Trinkle, First-principles data for solid-solution
strengthening of magnesium: From geometry and chemistry to properties,
Acta Mater. 58 (2010) 5704–5713.
- [20] S. Ganeshan, S. L. Shang, Y. Wang, Z.-K. Liu, Effect of alloying elements on
the elastic properties of Mg from first-principles calculations, *Acta Mater.*
680 57 (2009) 3876–3884.
- [21] Z.-K. Liu, H. Zhang, S. Ganeshan, Y. Wang, S. N. Mathaudhu, Computa-
tional modeling of effects of alloying elements on elastic coefficients, *Scripta*
Mater. 63 (2010) 686–691.
- [22] M. de Jong, D. L. Olmstead, A. van de Walle, M. Asta, First-principles
685 study of the structural and elastic properties of rhenium-based transition-
metal alloys, *Phys. Rev. B* 86 (2012) 224101–1–224101–9.
- [23] R. L. Fleisher, in *The Strengthening of Metals*, edited by D. Peckner, Rein-
hold, New York, 1964.

- [24] S. Takeuchi, Solid-solution strengthening in single crystals of iron alloys, J. Phys. Soc. Japan 27 (1969) 929–940.
- [25] S. F. Pugh, Relations between the elastic moduli and the plastic properties of polycrystalline pure metals, Phil. Mag. 45 (1954) 823–843.
- [26] H. K. Yeddu, A. Malik, J. Ågren, G. Amberg, A. Borgenstam, Three-dimensional phase-field modeling of martensitic microstructure evolution in steels, Acta Mater. 60 (2012) 1538–1547.
- [27] A. Srivastava, A. F. Bower, L. G. H. Jr., J. E. Carsley, L. Zhang, F. Abu-Farha, A multiscale approach to modeling formability of dual-phase steels, Modelling Simul. Mater. Sci. Eng. 24 (2016) 025011–1–025011–30.
- [28] F. Roters, P. Eisenlohr, L. Hantcherli, D. D. Tjahjanto, T. R. Bieler, D. Raabe, Overview of constitutive laws, kinematics, homogenization and multiscale methods in crystal plasticity finite-element modeling: Theory, experiments, applications, Acta Mater. 58 (2010) 1152–1211.
- [29] R. E. Smallman, A. H. W. Ngan, Modern Physical Metallurgy, 8th edition, Butterworth-Heinemann, Waltham, 2014.
- [30] O. Buck, L. A. Ahlberg, L. J. Graham, G. A. Alers, C. A. Wert, K. C. Hsieh, Harmonic and anharmonic elastic properties of the α -Nb–H system, Phys Status Solidi (a) 55 (1979) 223–230.
- [31] Y. S. Touloukian, R. K. Kirby, R. E. Taylor, P. D. Desai, Thermophysical Properties of Matter: Thermal Expansion - Metallic Elements and Alloys, Vol. 12, Plenum Press, 1975.
- [32] P. E. Busby, C. Wells, Diffusion of boron in alpha-iron, J. Met. 6 (1954) 972–972.
- [33] P. M. Strocchi, B. A. Melandri, A. Tamba, On the nature of boron solid solution in α -iron, Nuovo Cimento B 51 (1967) 1–11.

- 715 [34] D. H. R. Fors, G. Wahnström, Nature of boron solution and diffusion in α -iron, Phys. Rev. B 77 (2008) 132102–1–132102–4.
- [35] S. S. Baik, B. I. Min, S. K. Kwon, Y. M. Koo, Boron solution and distribution in α -Fe: Application to boron steel, Phys. Rev. B 81 (2010) 144101–1–144101–7.
- 720 [36] V. Savic, J. L. G. Hector, H. Ezzat, A. Sachdev, J. Quinn, R. Krupitzer, X. Sun, Integrated computational materials engineering (ICME) for third generation advanced high-strength steel development, SAE technical paper 2015-01-0459.
- [37] A. Zunger, S.-H. Wei, L. G. Ferreira, J. E. Bernard, Special quasirandom structures, Phys. Rev. Lett. 65 (1990) 353–356.
- 725 [38] S.-H. Wei, L. G. Ferreira, J. E. Bernard, A. Zunger, Electronic properties of random alloys: Special quasirandom structures, Phys. Rev. B 42 (1990) 9622–9650.
- [39] J. F. Nye, Physical Properties of Crystals: Their Representation by Tensors and Matrices, Oxford University Press, Oxford, 1985.
- 730 [40] B. B. Karki, L. Stixrude, S. J. Clark, M. C. Warren, G. Ackland, J. Crain, Structure and elasticity of MgO at high pressure, Am. Mineral. 82 (1997) 51–60.
- [41] B. B. Karki, G. J. Ackland, J. Crain, Elastic instabilities in crystals from *ab initio* stress-strain relations, J. Phys.: Condens. Matter 9 (1997) 8579–8589.
- 735 [42] X.-F. Li, G.-F. Ji, F. Zhao, X.-R. Chen, D. Alfè, First-principles calculations of elastic and electronic properties of NbB₂ under pressure, J. Phys.: Condens. Matter 21 (2009) 025505–1–025505–7.
- 740 [43] D. R. Trinkle, Lattice and elastic constants of titanium-niobium monoborides containing aluminum and vanadium, Scripta Mat. 56 (2007) 273–276.

- [44] G. Kresse, J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169–11186.
- [45] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865–3868.
- [46] P. E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953–17979.
- [47] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Phys. Rev. B 59 (1999) 1758–1775.
- [48] H. J. Monkhorst, J. D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B 13 (1976) 5188–5192.
- [49] D. J. Singh, L. N. (eds.), Planewaves, Pseudopotentials, and the LAPW Method, 2nd edition, Springer, New York, 2006.
- [50] M. Methfessel, A. T. Paxton, High-precision sampling for Brillouin-zone integration in metals, Phys. Rev. B 40 (1989) 3616–3621.
- [51] P. E. Blöchl, O. Jepsen, O. K. Andersen, Improved tetrahedron method for Brillouin-zone integrations, Phys. Rev. B 49 (1994) 16223–16233.
- [52] M. J. Mehl, B. M. Klein, D. A. Papaconstantopoulos, in Intermetallic Compounds: Principles and Practice, Volume I: Principles, edited by J. H. Westbrook and R. L. Fleischer, John Wiley and Sons, London, 1995.
- [53] B. Fornberg, Generation of finite difference formulas on arbitrarily spaced grids, Math. Comp. 51 (1988) 699–706.
- [54] G. Y. Guo, H. H. Wang, Gradient-corrected density functional calculation of elastic constants of Fe, Co and Ni in bcc, fcc, and hcp structures, Chinese J. Phys. 38 (2000) 949–961.

- [55] S. L. Frederiksen, K. W. Jacobsen, Density functional theory studies of screw dislocation core structures in bcc metals, *Phil. Mag.* 83 (2003) 365–375.
- 770
- [56] K. J. Caspersen, A. Lew, M. Ortiz, E. A. Carter, Importance of shear in the bcc-to-hcp transformation in iron, *Phys. Rev. Lett.* 93 (2004) 115501–1–115501–4.
- [57] L. Ventelon, F. Willaime, Generalized stacking-faults and screw-dislocation core-structure in bcc iron: A comparison between *ab initio* calculations and empirical potentials, *Phil. Mag.* 90 (2009) 1063–1074.
- 775
- [58] J. A. Rayne, B. S. Chandrasekhar, Elastic constants of iron from 4.2°K to 300°K, *Phys. Rev.* 122 (1961) 1714–1716.
- [59] C. A. Rotter, C. S. Smith, Ultrasonic equation of state of iron. i. low pressure, room temperature, *J. Phys. Chem. Solids* 27 (1966) 267–276.
- 780
- [60] M. W. Guinan, D. N. Beshers, Pressure derivatives of the elastic constants of α -iron to 10 Kbs, *J. Phys. Chem. Solids* 29 (1968) 541–549.
- [61] H. Kim, D. R. Trinkle, Effect of charge on point defect size misfits from *ab initio*: Aliovalently doped SrTiO₃, *Comp. Mat. Sci.* 119 (2016) 41–45.
- [62] M. R. Fellingner, L. G. Hector, Jr., D. R. Trinkle, Data files for *ab initio* calculations of the lattice parameter and elastic stiffness coefficients of bcc Fe with solutes, Data in Brief *submitted*.
- 785
- [63] G. Grimvall, *Thermophysical Properties of Materials*, 2nd edition, North Holland, 1999.
- [64] G. Wang, S. Shönecker, S. Hertzman, Q.-M. Hu, B. Johansson, S. K. Kwon, L. Vitos, *Ab initio* prediction of the mechanical properties of alloys: The case of Ni/Mn-doped ferromagnetic Fe, *Phys. Rev. B* 91 (2015) 224203.
- 790

Figure 1: (color online). Convergence of pure bcc Fe properties with respect to k -point sampling. We compute the energy per atom, lattice parameter a_0 , bulk modulus B_0 , shear modulus C'_0 , and elastic stiffness coefficients C^0_{ij} , and the elastic moduli and stiffness coefficient derivatives with respect to a using three different k -point meshes. We use $N_k \times N_k \times N_k$ Γ -centered and shifted Monkhorst-Pack [48] meshes for the bcc lattice. These individual meshes are fcc meshes of points in k -space, which form a denser simple cubic mesh of points when combined together. The individual meshes lead to slower convergence with respect to k -points than the combined meshes for all the properties. This is especially pronounced for the elastic stiffness coefficient derivatives, which show large oscillations with respect to k -points for the individual Monkhorst-Pack meshes.

Figure 2: (color online). Workflow for computing solute strain misfits and elastic stiffness coefficient derivatives with respect to solute concentration. The arrows show which outputs from a given calculation are inputs to other calculations. The green boxes within each section represent sets of DFT calculations and post-processing of the DFT data. The yellow boxes represent steps in which no DFT calculations are performed, but use DFT results from prior steps in the workflow to calculate properties.

Figure 3: (color online). Strain misfit tensor values for substitutional (left) and octahedral interstitial (right) solutes. We compute the tensors using $2 \times 2 \times 2$ (16 lattice sites), $3 \times 3 \times 3$ (54 lattice sites), and $4 \times 4 \times 4$ (128 lattice sites) supercells to examine convergence with respect to finite-size effects. The supercells contain a single solute which yields solute concentrations of 6.25, 1.85, and 0.78 at.%, respectively. The misfit tensors for the substitutional solutes are isotropic so $\epsilon_{ii}^s = \overline{\epsilon^s}$, whereas the misfit tensors are anisotropic for the interstitial solutes. The strongest finite-size effects occur for Mn, which has a small negative strain misfit value for the $2 \times 2 \times 2$ supercell and larger positive values for the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells. This behavior is reflected by the Mn magnetic moment which changes from +0.9 in the $2 \times 2 \times 2$ supercell to -2.0 in the larger supercells. The strain misfits for interstitial C and N are an order of magnitude larger than the substitutional strain misfits due to the large stress they induce in the bcc lattice. The data in the figure is for atomic concentration. For atomic percent, the values must be divided by 100.

Figure 4: (color online). Single-crystal elastic stiffness coefficient derivatives with respect to solute concentration for $2 \times 2 \times 2$ (16 lattice sites), $3 \times 3 \times 3$ (54 lattice sites), and $4 \times 4 \times 4$ (128 lattice sites) supercells. The supercells contain a single solute which yields solute concentrations of 6.25, 1.85, and 0.78 at.%, respectively. We compute volumetric and chemical contributions to the C_{ij} derivatives separately and sum them to give total derivatives. We also compute the total derivatives directly using fully relaxed supercells containing solutes. Each supercell size for each solute has three bars in the figure: one for the volumetric effect, one for the chemical effect, and one for the direct calculations. The volumetric and chemical bars are stacked on each other when they have the same sign so that the total change is the combined length of both bars. When the terms have opposite signs, the larger bar is shifted vertically so that the bars overlap to demonstrate the partial cancellation of the two effects. The small arrows indicate the sums of the volumetric and chemical contributions, which agree well with the directly computed derivatives. The disagreement for the smallest supercell size in some cases indicates finite size effects. The data in the figure is for atomic concentration. For atomic percent, the values must be divided by 100.

Figure 5: (color online). Computed changes in the Voigt-Reuss-Hill polycrystalline shear modulus G and Young's modulus E due to Mn and C solutes compared to experimental data. The DFT results labeled “analytic” are lines with slopes given by Eqn. A.15 and Eqn. A.16 in the Appendix, with numerical values given in Table 1. The DFT results labeled “FD” are finite difference changes in G and E computed from the single-crystal C_{ij} from the $4 \times 4 \times 4$ and $3 \times 3 \times 3$ supercells using Eqn. A.8 and Eqn. A.9. These C_{ij} values equal $C_{ij}^0 + (\partial C_{ij} / \partial c_s)_{\text{tot}} \cdot c_s$, where we use the $(\partial C_{ij} / \partial c_s)_{\text{tot}}$ values computed for each supercell size. The $4 \times 4 \times 4$ supercells have $c_s = 0.78$ at.% and the $3 \times 3 \times 3$ supercells have $c_s = 1.85$ at.%. The dashed lines connecting the FD points are guides for the eye. The variation in the FD results between the two supercell sizes is due to the small variations in the C_{ij} computed using these different supercell sizes. The analytic results are derived from the fitted C_{ij} derivative values in Table 1 which smooth out these variations. The DFT results agree with the trends in the experimental data from Speigh *et al.* [6] which show that these solutes cause both moduli to decrease, with C producing a larger effect on each modulus than Mn. The dotted lines connecting the experimental data points are guides for the eye.