

***Ab initio* relaxation volumes of transition metal solutes in iron and tungsten**

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Atomic volume differences determine the structure and phase stability of alloys. To assess the size mismatch, atomic volumes of pure elements, derived from their elemental crystalline states, are normally used as a reference. Using *ab initio* calculations, we show that substitutional transition metal solute atoms in bcc iron or tungsten exhibit sizes substantially different from their elemental volumes. Analysis of electronic structure suggests that the significant oversizing of substitutional solutes in bcc α -iron is caused by the asymmetric filling of electronic states of solute atoms. This produces a strong local magnetovolume effect where, for example, the apparent sizes of platinum and palladium solute atoms are from 35% to 40% larger than their elemental volumes. The analysis of nonlocal variation of electronic structure in the neighborhood of a solute atom shows that in bcc tungsten, the atoms near a substitutional $3d$ transition metal solute atom shrink, whereas in bcc iron, atoms next to a substitutional site swell, further increasing the apparent relaxation volume of the solute atom. Constrained magnetic DFT calculations show that manganese, iron, and cobalt solute impurity atoms in tungsten retain their magnetic moments, with collinear spin-flip barriers of 0.20, 0.52, and 0.17 eV, respectively. In other instances, elements like Cr in α -Fe are nominally undersized if the elemental volumes are compared, but in a solute form the relaxation volume of Cr is positive (+20% of its atomic volume), stemming from the electron transfer effect and variation of the effective volume of neighboring host Fe atoms. Simulations suggest that application of strong magnetic field might also affect the relaxation volume of transition metal solutes and their solubility.

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I. INTRODUCTION

Body-centered cubic (bcc) transition metals and their alloys are industrial materials of broad technological significance [1,2]; this includes their applications in engineering for extreme environments. Iron, iron alloys, steels, and tungsten are candidate materials for structural and plasma-facing components of fusion power plants [3,4], where ferritic and ferritic/martensitic (F/M) iron-chromium steels exhibit particularly good structural stability under irradiation [4–7]. Tungsten and its alloys are refractory metals with high melting points, making them suitable for a variety of high-temperature applications [8].

Solute elements strongly affect mechanical and structural properties of metals, including their hardness, toughness, and ductility [9]. In steels, a broad variety of properties can be

modified by tailoring the type and content of the solutes. Solute atoms may be introduced by design or unintentionally during manufacturing. The presence of even low concentration of solutes can alter the structure [10], phase stability [11,12], elastic stiffness coefficients [13–15], stacking fault energies [11,16,17], creep resistance, and even the symmetry of dislocation cores [18]. The presence of very low, effectively undetectable, concentration of impurities may have a strong effect on transport properties of materials, altering the equilibrium vacancy concentration [19]. Magnetic impurities in nonmagnetic metals produce highly unusual resistivity effects driven by dynamic electronic fluctuations, reviewed in Refs. [20,21].

Ab initio calculations, based on density functional theory (DFT), provide accurate information about the group-dependent variation of properties of pure metals [22,23] as well as about point defects in those metals [24–28]. DFT has also been applied to studying the interaction of solutes with defects [7,29,30], dislocations [18,31–33], and grain boundaries [34]. *Ab initio* calculations are able to quantify the solute-dependent variation of the lattice parameter [32,35] and elastic stiffness constants [14,35]. Using this information, simulations can predict solid-solution alloy strengthening [33], changes to ductility [36], and yield strength [37]. Many properties, affecting the structural stability of complex alloys, particularly the transition from a crystalline to a bulk metallic glass state, are correlated with the volume misfit between atoms in an alloy [38,39]. Magnetism of solute atoms and/or the alloy matrix is also an important factor, requiring attention in the context of modeling multicomponent Fe, Ni, Mn, and Cr alloys [40].

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The main factors controlling the structure of alloys are the atomic size misfit, the relative valence factor, and electron concentration [41,42]. Nabarro [43] discussed the internal strain developing during precipitation in alloys, treating it as a solute size effect. Atomic volume is a fundamental quantity in condensed matter physics and metallurgy. It provides a starting point for evaluating other quantities, such as the heat capacity at constant volume, the Leibfried and Bragg numbers, the Debye temperature from the Lindemann equation, and the Grüneisen constant [44]. Relative atomic volumes (size factors), through empirical Hume-Rothery rules, define the basic conditions for which one element may be soluble in another [45]. These rules state that if the solute volume differs by more than 15% from the volume of the solvent, the size factor is unfavorable and solubility is likely to be low [9]. Such criteria have been recently extended and exploited technologically in the analysis of high-entropy alloys [38,39,46], where some even more stringent conditions for solubility and crystalline phase formation were identified.

Alloys containing oversized solutes have been selected for designing radiation resistant materials for nuclear applications. Oversized solute additions appear to prolong the incubation period for void nucleation, suppressing void growth [47,48], and delaying the radiation-induced segregation of Cr from Ni at grain boundaries in 316L austenitic steels [49].

Atomic size trends in pure transition metals are well understood and can be derived from the consideration of their partially filled $(n-1)d$ subshells, where n is the principal quantum number. According to the Madelung ordering rules for the neutral ground state, the d electron band is filled after the ns shell is fully occupied. As the group number increases within a given period, the number of protons and electrons in the metal also increases. The electrons progressively populate the unfilled $(n-1)d$ subshells, increasing the screening of nuclear charge for the outer ns electrons. The effective size of a transition metal atom decreases as a function of group number, albeit to a lesser extent than in nontransition metals where electrons are added to the outer shell and do not screen the increased nuclear charge.

For transition metal series $4d$ and $5d$, the metals in each group have similar sizes due to the so-called Lanthanide contraction [50]. Lanthanide elements preceding the sixth period exhibit a steady volumetric contraction with increasing group number due to the filling of $4f$ orbitals that provide little screening of the nuclear charge to the valence electrons. At the end of the Lanthanide series, the atomic radii shrink to a size comparable with Zr. The electrons, populating the $5d$ bands, provide a similar degree of screening to nuclear charges as the $4d$ electrons.

The objective of this paper is to perform a quantitative *ab initio* investigation of the misfit size effects of transition metal solutes in bcc ferromagnetic Fe and bcc W. We find that the volumes of transition metal solutes in Fe and W are anomalous relative to their values in elemental crystalline forms. The origin of the anomalous solute size effect stems from changes in the local electronic structure associated both with the solute atoms themselves as well as with their nearest-neighbor environment.

In ferromagnetic iron, using a constrained DFT, we also examine the magnetovolume effect. This effect contributes to the variation of the volume of a solute in the host matrix. By analyzing the local density of states (LDOS) from electronic structure calculations, we find that changes in the occupancy of states in the atoms neighboring the substitutional site cause these atoms to either shrink or swell, contributing to the observed relaxation volume of a solute. We also evaluate the enthalpy of mixing and compare it to experiment and earlier calculations.

The paper is structured as follows. We start by outlining a general approach to the computationally efficient *ab initio* evaluation of relaxation volumes of substitutional atoms. Then we compare the relaxation volumes, computed using *ab initio* methods, with atomic volume data derived from elemental compounds and chemical atomic radii. We briefly summarize the principles of constrained magnetic moment calculations in the context of atomic strain relaxation analysis.

Applying the methodology to a variety of impurity elements in bcc iron and tungsten, we focus on the unusually large strain relaxation effects found in bcc Fe, where the observed large relaxation volume effects stem from changes in the local electronic structure and electron correlation effects, fundamentally responsible for the ferromagnetism and structural stability of iron. We evaluate enthalpies of mixing and energies of solution for various impurity atoms, spanning the Periodic Table, and discuss the significance of accurate assessment of atomic size effects in the context of Hume-Rothery rules of formation of metallic alloys.

II. METHODOLOGY

A. Density functional theory

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [51–54] version 5.4.1. All calculations included spin polarization and used the projector augmented wave (PAW) formalism [55,56] with the exchange-correlation functional approximated by the generalized gradient approximation (GGA) functional by Perdew, Burke, and Ernzerhof (PBE) [57,58]. The pseudopotentials used in the calculations are listed in Table I. Calculations were repeated on a selection of groups IV, VI, VII, VIII, and X transition metal atoms with the meta-GGA functional r^2 SCAN [59,60], the results of which are compared with our PBE simulations in Sec. III A. Plane waves were used to construct the electronic basis set with the cutoff energy of 400 eV.

The calculations use supercells containing either 250 Fe or W atoms. Each supercell contains $5 \times 5 \times 5$ bcc cubic unit cells. Fe is initialized to be ferromagnetic and W non-magnetic. We used a $3 \times 3 \times 3$ k-point mesh set according to the Monkhorst-Pack method [61]. The Methfessel-Paxton broadening scheme [62] was used, with the width of smearing of 0.3 eV. The convergence criteria for the self-consistent field were set to 10^{-8} eV and the maximum ionic force to 10^{-4} eV/Å. The simulation cell is relaxed to stress-free conditions according to the DIIM method [63,64]. The calculated lattice constant of Fe is 2.831 Å and W is 3.172 Å.

TABLE I. The header of the PAW pseudopotentials and the number of valence electrons (VEs for all elements included in this study.

Element	Header of the PAW potential	VEs
Ag	PAW_PBE Ag 02Apr2005	11
Au	PAW_PBE Au 04Oct2007	11
Co	PAW_PBE Co 02Aug2007	9
Cr	PAW_PBE Cr 06Sep2000	6
Cu	PAW_PBE Cu 22Jun2005	11
Fe	PAW_PBE Fe 06Sep2000	8
Hf	PAW_PBE Hf 20Jan2003	4
Ir	PAW_PBE Ir 06Sep2000	9
Mn	PAW_PBE Mn 06Sep2000	7
Mo	PAW_PBE Mo 08Apr2002	6
Nb	PAW_PBE Nb_pv 08Apr2002	11
Ni	PAW_PBE Ni 02Aug2007	10
Os	PAW_PBE Os 17Jan2013	8
Pd	PAW_PBE Pd 04Jan2005	10
Pt	PAW_PBE Pt 04Feb2005	10
Re	PAW_PBE Re 17Jan2003	7
Rh	PAW_PBE Rh 04Feb2005	9
Ru	PAW_PBE Ru 04Feb2005	8
Ta	PAW_PBE Ta 17Jan2003	5
Tc	PAW_PBE Tc 04Feb2005	7
Ti	PAW_PBE Ti 08Apr2002	4
V	PAW_PBE V 08Apr2002	5
W	PAW_PBE W 08Apr2002	6
Zr	PAW_PBE Zr 04Jan2005	12

Subsequently, the dimensions of each supercell remain fixed. One host atom is replaced by a substitutional atom, where the substitutional atom is a transition metal atom from groups 4–11. This corresponds to a dilute alloy limit with the solute concentration of 0.4%. After replacing a host atom with a solute, the atomic configuration is relaxed, keeping the boundaries of the supercell fixed, to a maximum ionic force lower than 10^{-3} eV/Å.

In addition, for all the transition metals, we computed atomic volumes for various crystal structures. We created body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close-packed (hcp) unit cells containing 2, 4, and 2 atoms, respectively. We have also calculated the atomic volume of Mn in the A12 structure. The k-point spacing of at least $0.15 \text{ \AA}^{-1}$ was used in each calculation. Volumes of the cells were relaxed to stress-free condition. The resulting elemental atomic volumes are summarized in Table II.

B. Elastic dipole tensor and elastic correction to energy

Macroscopic stress detected at the boundaries of a simulation cell equals the average internal stress in the cell:

$$\bar{\sigma}_{ij} = \frac{1}{V_{\text{cell}}} \int \sigma_{ij} dV, \quad (1)$$

where V_{cell} is the cell volume. The elastic dipole tensor P_{ij} of a spatially localized lattice defect, in this instance a substitutional atom, can be evaluated from the stress developing in the simulation cell as [71–73]

$$P_{ij} = V_{\text{cell}} (C_{ijkl} \epsilon_{kl}^{\text{app}} - \bar{\sigma}_{ij}), \quad (2)$$

where V_{cell} is the volume of the simulation cell and C_{ijkl} is the tensor of stiffness constants [74] for the host lattice. Since dimensions of the simulation cells are fixed, there is no applied strain $\epsilon_{kl}^{\text{app}} = 0$. A correction to the formation energy due to elastic interaction between periodic images of the defect under periodic boundary conditions can be evaluated from the elastic dipole tensor of the defect and anisotropic elastic Green's function [26,72]. The periodic image interaction energy correction was computed using the CALANIE code [75].

Since values of elastic constants are required as input for evaluating elastic Green's function, we computed these constants using the Le Page and Saxe method [76]. Calculations were performed using 2-atom simulation cells and a $15 \times 15 \times 15$ k-point grid. The computed bulk properties are listed in Table III. The calculated elastic constants are in good agreement with the corresponding experimental values [9,77–79].

C. Relaxation volume and metallic radius

The relaxation volume tensor Ω_{ij} of a defect or a substitutional atom is a fundamental parameter of a defect structure. It characterizes the change of shape and volume of a sample following the creation of a defect. It is related to the elastic dipole tensor of a defect through its convolution with the elastic compliance tensor S_{ijkl} :

$$\Omega_{ij} = S_{ijkl} P_{kl}, \quad (3)$$

where $\mathbf{S} = \mathbf{C}^{-1}$, satisfying the condition [74,80] $C_{ijkl} S_{klmn} = \frac{1}{2}(\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm})$. The relaxation volume of a defect is equal to the trace of the relaxation volume tensor:

$$\Omega^{\text{rel}} = \text{Tr}(\Omega_{ij}) = \Omega_{11} + \Omega_{22} + \Omega_{33}. \quad (4)$$

It provides a scalar measure of local contraction or expansion of the lattice.

As a simple illustration, the relaxation volume of a vacancy is negative whereas the relaxation volume of a self-interstitial atom is positive [26,27,73,81]. Randomly distributed vacancies produce tensile strain in the lattice, giving rise to lattice contraction and the effective increase of the average lattice parameter [82], whereas self-interstitial atom (SIA) defects, giving rise to internal compressive strains, reduce the observed average lattice parameter [83]. The relaxation volume of a defect has proven to be a remarkably universal concept for studying and characterization of defects [26,28,71,73,81,83–89].

Using Eqs. (1)–(4), we express the volume of a solute atom in a host lattice as

$$\Omega_{\text{host}}^{\text{sol}} = \Omega_0 + \Omega^{\text{rel}}, \quad (5)$$

where Ω_0 is the atomic volume of the host solvent, in the bcc phase, and Ω^{rel} is the relaxation volume of the substitutional solute atom.

Since the outermost electron in a transition metal occupies an s orbital, a reasonable approximation of its volume can be given by its metallic volume

$$V^{\text{met}} = \frac{4}{3} \pi r_{\text{met}}^3, \quad (6)$$

where the metallic radius r_{met} is determined from the lattice constant of a pure metal in its ground state [42]. The distances between the first-nearest neighbors (NNs) in ideal

TABLE II. The ground state crystal structure (CS); volumes of pure transition metal (TM) atoms in bcc Ω_{bcc} , fcc Ω_{fcc} , and hcp Ω_{hcp} phases; and the metallic radii (r_{met}) and metallic volumes (V^{met}) for each transition metal upon substitution into Fe and W. Metallic radii are calculated from the ground state crystal structure using the Goldschmidt correction. Volumes are normalized per atom. Daggered elements have magnetic allotropes whose configurations are labeled (1) for ferromagnetic (FM), (2) for single-layer antiferromagnetic (AFM-SL), or (3) for double-layer antiferromagnetic (AFM-DL). The lowest energy magnetic configurations for Cr and Mn are experimentally determined as a spin density wave [65–67] and a noncollinear antiferromagnetic [68] state, respectively. Still, the energy difference with their collinear antiferromagnetic configurations [69] is almost indistinguishable in DFT. The volume per atom of collinear AFM α -Mn (Ω_{A12}) is 11.13 Å³.

TM	CS	Ω_{bcc} (Å ³)	Ω_{fcc} (Å ³)	Ω_{hcp} (Å ³)	r_{met} (Å)	r_{met} (Å) [70]	V^{met} (Å ³)
3d							
Ti	hcp	16.951	17.100	17.104	1.43	1.47	12.221
V	bcc	13.212	13.662	13.645	1.33	1.34	9.846
Cr [†]	bcc	11.631 ⁽²⁾	11.752	11.764	1.27	1.28	8.668
Mn [†]	a12	10.858 ⁽¹⁾	11.304 ⁽²⁾	10.633 ⁽²⁾		1.27	
Fe [†]	bcc	11.333 ⁽¹⁾	11.167 ⁽³⁾	10.149	1.26	1.26	8.446
Co [†]	hcp	11.008 ⁽¹⁾	10.839 ⁽¹⁾	10.792 ⁽¹⁾	1.23	1.25	7.711
Ni [†]	fcc	10.942 ⁽¹⁾	10.855 ⁽¹⁾	10.909 ⁽¹⁾	1.24	1.24	8.038
Cu	fcc	12.010	11.951	12.022	1.28	1.28	8.849
4d							
Zr	hcp	22.773	23.168	23.073	1.58	1.60	16.486
Nb	bcc	17.928	18.499	18.207	1.47	1.46	13.361
Mo	bcc	15.587	15.866	15.825	1.40	1.39	11.617
Tc	hcp	14.430	14.350	14.281	1.35	1.36	10.204
Ru	hcp	14.098	13.716	13.640	1.33	1.34	9.746
Rh	fcc	14.354	13.936	13.996	1.35	1.34	10.319
Pd	fcc	15.350	15.232	15.394	1.39	1.37	11.279
Ag	fcc	17.983	17.811	17.901	1.47	1.44	13.189
5d							
Hf	hcp	22.049	22.299	22.273	1.56	1.59	15.914
Ta	bcc	18.092	18.640	18.577	1.48	1.46	13.483
W	bcc	15.949	16.241	16.200	1.42	1.39	11.886
Re	hcp	15.011	14.967	14.936	1.37	1.37	10.672
Os	hcp	14.718	14.291	14.218	1.34	1.35	10.159
Ir	fcc	15.077	14.498	14.571	1.37	1.36	10.736
Pt	fcc	15.737	15.559	15.719	1.40	1.39	11.521
Au	fcc	17.943	17.868	18.011	1.47	1.44	13.231

bcc, fcc, and hcp configurations are $d_1^{\text{bcc}} = \sqrt{3}a^{\text{bcc}}/2$, $d_1^{\text{fcc}} = \sqrt{2}a^{\text{fcc}}/2$, and $d_1^{\text{hcp}} = a^{\text{hcp}}$, respectively. The metallic radius is half the shortest distance between the neighboring atoms. To ensure consistency with the treatment of alloys, it is necessary to bring the atomic radii into a common framework [42]. It is expected that a smaller coordination number results in

a smaller interatomic distance. The Goldschmidt correction [42,90] adjusts the radii of structures with coordination numbers smaller than 12 to an empirical 12-coordination radius giving the same volume. In this approach, the relative radius of a bcc metal is $0.97r_{\text{met}}$. Hence, the metallic radius for a bcc structure is defined as $r_{\text{met}} = d_1^{\text{bcc}}/(2 \times 0.97)$.

TABLE III. Elastic constants C_{ij} in Voigt notation, the atomic volume Ω_0 , the equilibrium lattice parameter a_0 , and the equilibrium magnetic moment M_0 of Fe and W calculated using VASP. Elastic constants were evaluated using the Le Page and Saxe method [76]. Experimental values of elastic constants were taken from Ref. [77] for Fe and Ref. [78] for W whereas values of the lattice constant were taken from Ref. [79]. The magnetic moment of Fe is taken from Ref. [9].

	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	Ω_0 (Å ³)	a_0 (Å)	M_0 (μ_B)
Fe	277.45	154.26	102.15	11.34	2.83	2.20
Exp	243.1	138.1	121.9	11.82	2.87	2.2
W	527.51	211.44	138.05	15.95	3.17	0.00
Exp	522.4	204.4	160.6	15.76	3.16	0.00

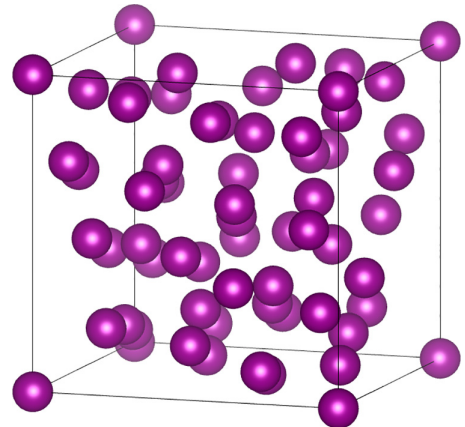


FIG. 1. Atomic configuration of the A12 structure of α -Mn.

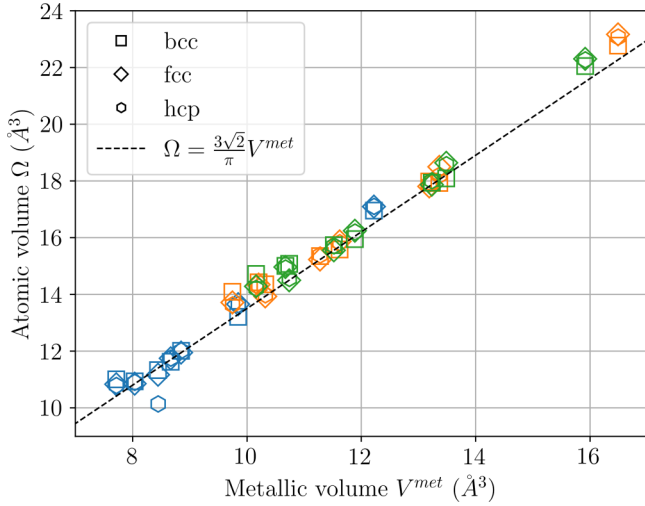


FIG. 2. Plot of atomic volume of element X in crystal structure CS, Ω_{CS}^X , against metallic volume, V^{met} , derived from the ground state structure of X. Hcp Fe is the most significant outlier (blue hexagon at $V^{\text{met}} \sim 8.4 \text{ \AA}^3$) and Mn is not included as the A12 structure has an ill-defined metallic radius. Most of the data lie close to the fit given by the dotted line due to the bcc, fcc, and hcp allotropes of a given element possessing similar atomic volumes. 3d, 4d, and 5d series metals are colored blue, orange, and green, respectively.

The A12 crystal structure shown in Fig. 1 represents the ground state atomic configuration of Mn [68]. The A12 structure has a lower symmetry compared to the bcc, fcc, or hcp phases typical of transition metals. It has an undefined coordination number [91], so we ignore the metallic radius of Mn and use its atomic volume in our figures instead.

We define the relative metallic atomic volume as

$$\Delta V_{\text{host}}^{\text{sol}} = \frac{V_{\text{sol}}^{\text{met}} - V_{\text{host}}^{\text{met}}}{V_{\text{host}}^{\text{met}}}. \quad (7)$$

The quantity characterizes a degree of misfit between metallic volumes of a solute atom and an atom in the host metal. The definition of $\Delta V_{\text{host}}^{\text{sol}}$ has a form similar to that of the relaxation volume Ω^{rel} . However, the metallic volume of an atom is a measure of the size of an atom in its pure elemental form.

In addition to investigating the ground state properties, we performed additional DFT calculations of atomic volumes of pure metals in various crystal structures. The results are presented in Table II. We note that different definitions of atomic sizes should not be compared directly, e.g., clearly $\Omega_0^{\text{w}} \neq V_{\text{w}}^{\text{met}}$. However, an inspection of Table II reveals that across bcc, hcp, and fcc crystal structures for a given element, the atomic volume, and by extension the metallic radii, are similar to each other. Thus, as shown in Fig. 2, for *all* transition metals X and crystal structures CS, we find $\Omega_{CS}^X \approx 3\sqrt{2}/\pi V^{\text{met}} \sim 1.35V^{\text{met}}$. Given that $\Omega_{\text{bcc}}^X \sim \Omega_{\text{fcc}}^X \sim \Omega_{\text{hcp}}^X$, the $3\sqrt{2}/\pi$ prefactor is derived from assuming an ideal c/a ratio in the hcp crystal structure. Altogether, quantitatively similar measures of relative atomic size difference are obtained irrespectively of whether one adopts the metallic or atomic volume.

For magnetic elements Cr, Mn, Fe, Co, and Ni, care was taken to ensure that the volume was provided for the lowest energy magnetic configuration. Bcc Fe, bcc Mn, bcc Co, bcc

Ni, fcc Co, fcc Ni, hcp Co, and hcp Ni are ferromagnetic [69,92,93]. Bcc Cr, fcc Mn, and hcp Mn are single-layer antiferromagnets [69,92,94,95]. Finally, fcc Fe has the lowest energy in a double-layer antiferromagnetic state [92,96–98]. Calculations of the double-layer AFM state required an 8-atom unit cell.

Experimentally, the magnetic ground states of both α -Cr (bcc) and γ -Fe (fcc) are spin density waves [99,100], whereas α -Mn (A12) has a noncollinear antiferromagnetic configuration [68]. In DFT calculations, the energies of these ground states are close to the energy of collinear antiferromagnetically ordered states [101–103] used in this work. We note that fcc γ -Fe is not the ground state crystal structure of Fe and that it is only structurally stable at high temperatures in the range from 1185 K to 1664 K [104]. Analysis shows that the fcc γ -Fe phase owes its stability to a combined effect of atomic vibrations and dynamic magnetic fluctuations [97,105], confirmed by the fact that its range of stability is above the Curie temperature $T_C = 1043 \text{ K}$, where any long-range magnetic order is absent.

In the following sections, we examine the difference between relaxation volumes of various solutes and their relative metallic volumes. The differences stem from the effect of chemical environment. The metallic radii and metallic volumes computed for various transition metals using DFT are presented in Table II.

D. Constrained noncollinear density functional theory

To constrain the magnetic moment of a solute atom to a chosen direction and magnitude $\mathbf{M}_I^0$, we add a constraint field energy penalty term E_p to the total energy functional [106,107]:

$$E = E_0 + E_p, \quad (8)$$

$$= E_0 + \sum_I^{N_{\text{sol}}} \lambda (\mathbf{M}_I - \mathbf{M}_I^0)^2, \quad (9)$$

where λ is a weight parameter that steers the strength of enforcement of the constraint. We apply the constraint only to the solute atom. The magnitude and direction of magnetic moments of all the host atoms are free to relax in response to the constrained magnetic moment on the solute atom. The penalty energy E_p at the energy minimum can be analytically proven to be inversely proportional to λ [107]. Calculations were performed using various values of λ . λ is chosen in such a way that the change of the penalty energy is lower than 1 meV if λ is increased by 1 eV.

Within the DFT framework, there is ambiguity in the quantitative definition of an atomic magnetic moment. In this work, we define the magnetic moment of atom I using spatially varying magnetic density and write [107]

$$\mathbf{M}_I = \int_{\Omega_I} \mathbf{m}(\mathbf{r}) F_I(|\mathbf{r} - \mathbf{r}_I|) d\mathbf{r}, \quad (10)$$

where radius R_I of sphere Ω_I is chosen to match the Wigner-Seitz radius supplied in the VASP PAW pseudopotentials (RWIGS). This satisfies the condition that chosen spheres are large enough but do not overlap. The cutoff function is $F_I = \text{sinc}(x)$, where $x = \pi|\mathbf{r} - \mathbf{r}_I|/R_I$. This function varies

TABLE IV. Relaxation volume, volume of a solute atom including the relaxation effect, diagonal element of the relaxation volume tensor $\Omega_{\alpha\alpha}$, diagonal element of the dipole tensor $P_{\alpha\alpha}$, and the magnetic moment M of $3d$, $4d$, and $5d$ series transition metal substitutional atoms in bcc W. All the off-diagonal elements of the dipole tensors $P_{\alpha\beta}$ and the relaxation volume tensors $\Omega_{\alpha\beta}$ are zeros. The values were computed using a 250-atom cell containing a single substitutional atom. Daggered rows provide data for the nonmagnetic metastable states. Values for a vacancy are given in row $\square$.

X_W	Ω^{rel} ($\text{\AA}^3$)	Ω_W^X ($\text{\AA}^3$)	$\Omega_{\alpha\alpha}$ ($\text{\AA}^3$)	$P_{\alpha\alpha}$ (eV)	M_X (μ_B)
Ti	-0.479	15.470	-0.160	-0.947	0.000
V	-4.169	11.780	-1.389	-5.116	0.000
Cr	-6.108	9.840	-2.036	-7.496	0.000
Mn	-5.083	10.866	-1.694	-6.237	2.322
Mn [†]	-6.939	9.010	-2.312	-8.515	0.000
Fe	-5.395	10.554	-1.798	-6.620	2.385
Fe [†]	-7.007	8.941	-2.335	-8.599	0.000
Co	-3.742	12.207	-1.247	-7.399	1.559
Co [†]	-4.188	11.761	-1.396	-8.280	0.000
Ni	-3.730	12.219	-1.243	-7.375	0.000
Cu	-2.726	13.222	-0.909	-5.391	0.000
Zr	4.390	20.339	1.463	8.681	0.000
Nb	1.984	17.932	0.661	3.923	0.000
Mo	0.043	15.991	0.014	0.085	0.000
Tc	-1.479	14.470	-0.493	-2.924	0.000
Ru	-1.815	14.133	-0.605	-3.589	0.000
Rh	-1.354	14.594	-0.451	-2.678	0.000
Pd	-0.315	15.634	-0.105	-0.622	0.000
Ag	1.211	17.160	0.404	2.395	0.000
Hf	3.722	19.671	1.241	7.359	0.000
Ta	2.793	18.742	0.931	3.427	0.000
W	0.000	15.949	0.000	0.000	0.000
Re	-1.038	14.910	-0.346	-2.053	0.000
Os	-1.540	14.409	-0.513	-3.045	0.000
Ir	-1.079	14.869	-0.360	-2.134	0.000
Pt	-0.006	15.943	-0.002	-0.012	0.000
Au	1.662	17.610	0.554	3.286	0.000
$\square$	-5.619	10.329	-1.873	-11.111	

TABLE V. Relaxation volume, volume of a solute atom including the relaxation effect, diagonal element of the relaxation volume tensor $\Omega_{\alpha\alpha}$, diagonal element of the dipole tensor $P_{\alpha\alpha}$, and the magnetic moment M of $3d$, $4d$, and $5d$ series transition metal substitutional atoms in bcc Fe. All the off-diagonal elements of the dipole tensors $P_{\alpha\beta}$ and the relaxation volume tensors $\Omega_{\alpha\beta}$ are zeros. The values were computed using a 250-atom cell containing a single substitutional atom. Daggered rows provide data for the nonmagnetic metastable states. Values for a vacancy are given in row $\square$.

X_{Fe}	Ω^{rel} ($\text{\AA}^3$)	Ω_{Fe}^X ($\text{\AA}^3$)	$\Omega_{\alpha\alpha}$ ($\text{\AA}^3$)	$P_{\alpha\alpha}$ (eV)	M_X (μ_B)
Ti	3.777	15.110	1.259	4.635	-0.962
V	2.320	13.653	0.773	2.847	-1.402
Cr	2.255	13.588	0.751	2.767	-1.826
Mn	2.332	13.665	0.777	2.862	-2.127
Fe	0.000	11.333	0.000	0.000	2.192
Co	1.133	12.466	0.378	1.391	1.694
Ni	2.555	13.888	0.852	3.136	0.867
Cu	2.209	13.542	0.736	2.711	0.123
Zr	10.408	21.741	3.469	12.772	-0.445
Nb	8.032	19.365	2.677	9.857	-0.748
Mo	5.799	17.132	1.933	7.117	-0.824
Tc	4.690	16.023	1.563	5.756	-0.608
Ru	4.677	16.010	1.559	5.739	0.224
Rh	5.951	17.284	1.983	7.303	0.626
Pd	8.091	19.423	2.696	9.928	0.387
Ag	9.339	20.672	3.112	11.460	0.066
Hf	9.200	20.533	3.066	11.290	-0.579
Ta	7.360	18.692	2.453	9.031	-0.782
W	5.986	17.318	1.995	7.345	-0.784
Re	5.361	16.693	1.787	6.578	-0.629
Os	5.265	16.597	1.754	6.460	-0.12
Ir	6.492	17.825	2.163	7.966	0.406
Pt	8.663	19.996	2.887	10.631	0.397
Au	10.969	22.301	3.655	13.460	0.166
$\square$	-2.383	8.950	-0.794	-2.924	

Figures 3 and 4 show plots of solute atom relaxation volume against the absolute atomic volume difference

$$\delta\Omega_{\text{H}}^X := \Omega_0^X - \Omega_0^{\text{H}}, \quad (13)$$

where Ω_0^X denotes the atomic volume of solute X in its ground state crystal structure and the bcc host $\text{H} = \text{W}$ or Fe . It is immediately apparent that relaxation volumes are well approximated by $\delta\Omega_{\text{W}}^X$, particularly for $4d$ and $5d$ series, whereas Ω_{rel} are generally greater compared to $\delta\Omega_{\text{Fe}}^X$. The significant oversizing of solutes in Fe arises from magnetic effects, stemming from electron correlations, as we show below. It is also worth noting that group IV hcp metal solutes Ti, Zr, and Hf are systematically undersized in both W and Fe. This may be rationalized by considering the change in d -orbital occupancy and charge transfer from the group IV solute, as discussed in Sec. III D. The variations of Ω_{rel} , in relative units of Ω_0^{H} , as a function of group number in W and Fe are plotted in Figs. 5 and 6, respectively. Relative metallic volumes are also plotted in the same figures for comparison. We have also plotted the relative metallic volumes given in

smoothly and equals unity at the center of the sphere, where $|\mathbf{r} - \mathbf{r}_I| = 0$ and drops to zero at sphere's boundary, where $|\mathbf{r} - \mathbf{r}_I| = R_I$.

III. RESULTS

A. Misfit sizes

Relaxation volumes of solute transition metal in bcc tungsten and bcc iron are presented in Tables IV and V. The values of diagonal elements of the tensors are also given for completeness, bearing in mind that in a crystal of cubic symmetry, both the relaxation volume and elastic dipole tensor are diagonal and isotropic, namely,

$$\Omega_{\alpha\beta} = \frac{1}{3}\delta_{\alpha\beta} \text{Tr } \hat{\Omega} = \frac{1}{3}\delta_{\alpha\beta} \Omega^{\text{rel}}, \quad (11)$$

$$P_{\alpha\beta} = \frac{1}{3}\delta_{\alpha\beta} \text{Tr } \hat{P}. \quad (12)$$

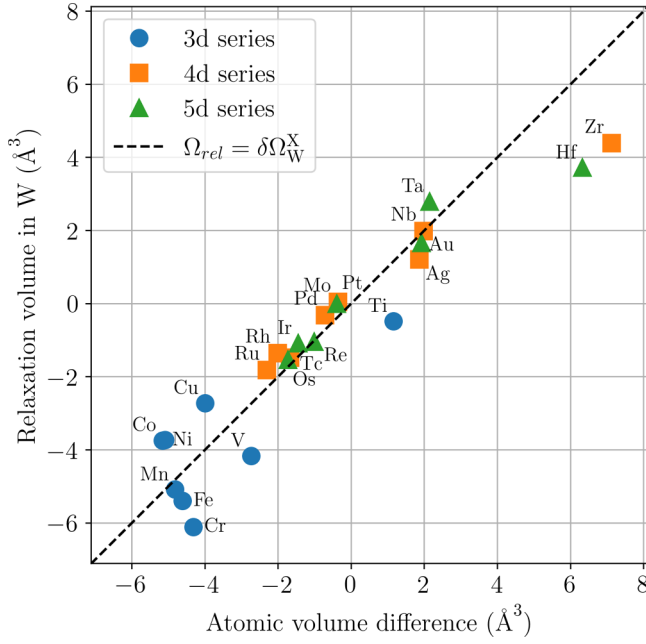


FIG. 3. Relaxation volume of a transition metal solute X in W plotted against the difference between atomic volumes of X and W, $\delta\Omega_W^X$, computed assuming the ground state crystal structure of both elements [cf. Eq. (13)]. In the majority of cases, solute relaxation volumes are consistent with the expected atomic volume differences.

Ref. [70] (labeled A) and relaxation volumes from Ref. [44] (labeled B).

In both iron and tungsten, the relaxation volumes of the 3d series solute atoms are significantly different from their relative metallic volumes. In the iron host lattice, the 3d

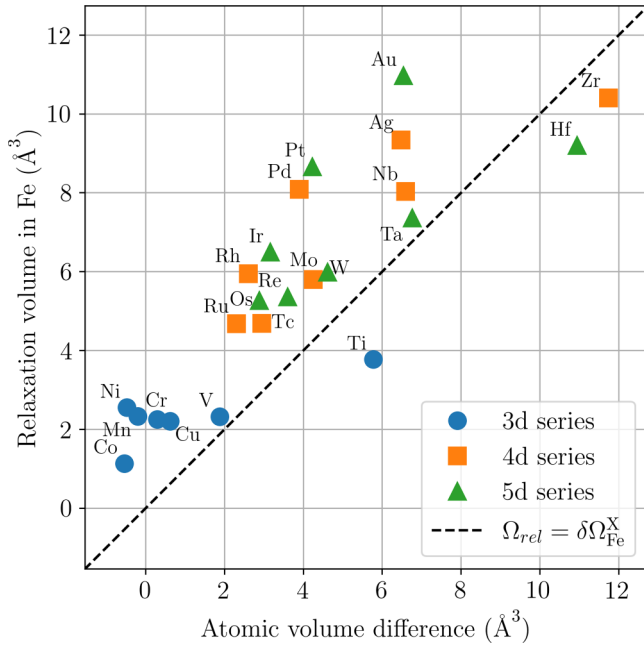


FIG. 4. Relaxation volume of transition metal solute X in Fe plotted against the difference between atomic volumes of X and Fe in their ground state phases, $\delta\Omega_{Fe}^X$ [cf. Eq. (13)]. Note that in the majority of cases, solute atoms are significantly oversized in comparison with expected atomic volume differences.

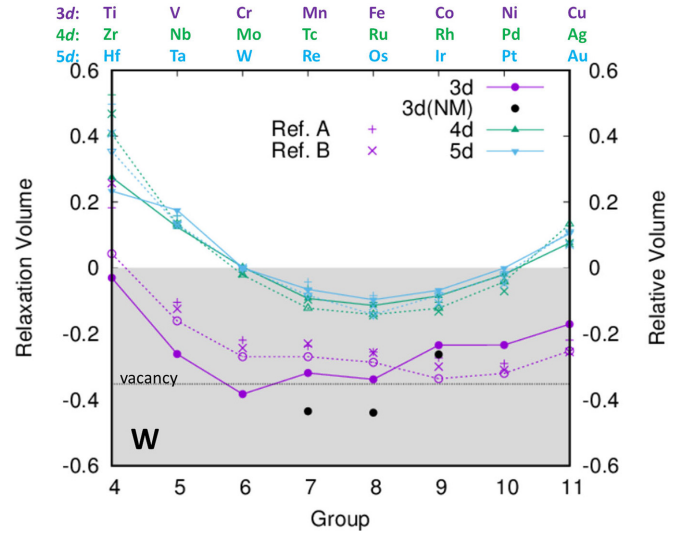


FIG. 5. Relaxation volume of a transition metal substitution in bcc W in the units of the host atomic volume Ω_0^W . Solid lines and symbols refer to relaxation volumes. Dashed lines with hollow symbols indicate the relative volume estimated from the metallic radii evaluated in this study. Tabulated values of Ω^{rel} are provided in Table IV. All the solutes relax to a nonmagnetic configuration with the exception of Mn_W , Fe_W , and Co_W , which maintain a nonzero magnetic moment. Their relaxation volumes in their nonmagnetic states are shown by solid black symbols. Relative volumes as per the metallic radii from Ref. [70] are represented by + and labeled A. Relative volumes determined from the atomic volumes of Ref. [44] are given by x, labeled B.

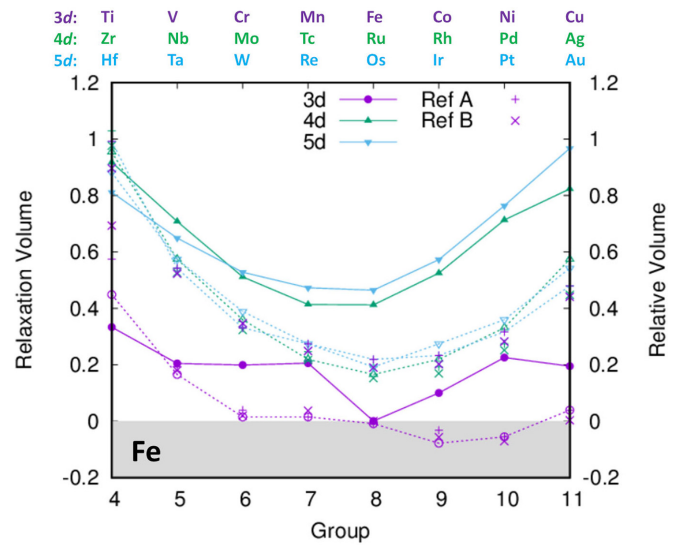


FIG. 6. Relaxation volumes of dilute transition metal substitutions in bcc Fe in the units of the host atomic volume Ω_0^{Fe} . Solid lines and symbols correspond to the relaxation volumes. Dashed lines with hollow symbols indicate relative volumes estimated from the metallic radii evaluated in this study. Values of Ω^{rel} are given in Table V. Relative volumes per the metallic radii from Ref. [70] are represented by + and labeled A. Relative volumes determined from the atomic volumes of Ref. [44] are given by x, labeled B.

transition metal solute atoms are anomalously oversized. On the other hand, in tungsten, they are generally undersized. This is consistent with the size factor estimates derived from earlier DFT studies [7]. Notably, Co and Ni, which are expected to be undersized in Fe, are calculated to be 10% and 22% larger than the host Fe atoms, respectively.

There are limited published data on relaxation volumes of solute atoms suitable for a meaningful comparison. Nonetheless, our calculated relaxation volume of $+0.20 \Omega_0$ for Cr_{Fe} is in excellent agreement with a recent study of defects and solute effects in concentrated Fe-Cr alloys [73] (symbol Cr_{Fe} here denotes a Cr atom in bcc Fe host lattice). To make a further comparison, we have evaluated relaxation volumes of a vacancy in both lattices. The relaxation volume of a vacancy in Fe is $-0.21 \Omega_0$, which agrees with the value of $-0.22 \Omega_0$ found in Ref. [26]. The relaxation volume of a vacancy in W is $-0.35 \Omega_0$, which agrees with the value of $-0.32 \Omega_0$ found in Refs. [84,86]. In Refs. [26,84,86], semicore pseudopotentials were used, accounting for the small differences between the computed values of vacancy relaxation volumes.

As expected from the group-specific trends in the periodic table, relaxation volumes of atoms in transition metal series 4d and 5d are similar in their magnitude due to the Lanthanide contraction for any given group. In the case of solute atoms in tungsten, relaxation volumes and relative metallic volumes agree within a few percent. However, when the 4d and 5d series elements are substituted into iron, the volumes are approximately up to 30% larger than expected from the metallic volume estimates. For example, a gold atom has the volume double the atomic volume of iron, according to the relaxation volume metric, whereas one would predict it to be only 50% larger than an Fe atom from the comparison of their metallic radii. Furthermore, in the dilute limit, platinum and palladium atoms in α -Fe appear to be oversized by nearly 40%; such anomalous behavior may have implications for their extensive applications as industrial catalysts.

To scrutinize our DFT calculations further, we repeated the computational procedure using semicore pseudopotentials that also include the p electrons treated as valence electrons. The results (not shown) are both qualitatively and quantitatively similar, indicating that p electrons make a negligible contribution to the anomalous substitutional atomic size effects addressed in this study.

As stated in Sec. II A, the relaxation volumes of some transition metals were reevaluated with the meta-GGA $r^2\text{SCAN}$ functional. Figures 7 and 8 provide a direct comparison of the predicted relaxation volumes between PBE and $r^2\text{SCAN}$ for W and Fe, respectively. In general, we find that systems containing magnetic elements bring about the largest discrepancies. In bcc W, Ω^{rel} is nearly identical for all elements except magnetic Cr and Fe. For the ferromagnetic host Fe, there is a systematic difference across all solute elements. While the trends are broadly preserved for the 4d and 5d series, magnetic 3d solutes Cr, Mn, and Ni contract the surrounding lattice, as opposed to solute oversizing predicted by the PBE functional. We note that both SCAN and $r^2\text{SCAN}$ are known to overestimate the magnetic moment and energy of Fe and other magnetic metals [108]. Therefore, we proceed to analyze the trends predicted by PBE in the subsequent sections of this paper. We note that the asymmetric filling of

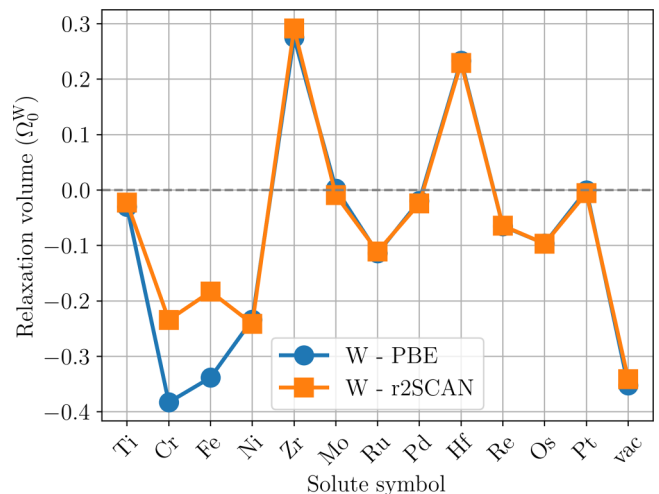


FIG. 7. Comparison of GGA PBE (blue circle) and meta-GGA $r^2\text{SCAN}$ (orange square) density functional predictions for a selection of transition metal relaxation volumes in bcc W. Volumes are given in the units of W atomic volume computed by relaxing a bcc unit cell in a calculation using the respective exchange correlation functionals.

spin states in magnetic 3d metals is driven by electron correlations. Therefore, the observed sensitivity of Ω^{rel} to various choices of electron exchange-correlation functionals confirms that magnetism is responsible for the significant unexpected variation of atomic volumes of solutes predicted by *ab initio* calculations.

In the following sections, we explore the origins of the observed misfit size effects.

B. The magnetovolume effect

The anomalous sizes of transition metal solutes in iron can likely be attributed to its magnetic properties [73,109–111].

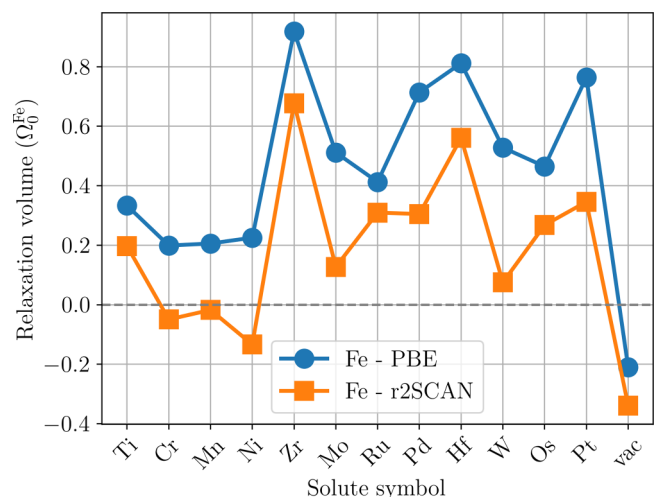


FIG. 8. Comparison of GGA PBE (blue circle) and meta-GGA $r^2\text{SCAN}$ (orange square) functional predictions for a selection of transition metal relaxation volumes in bcc Fe. Volumes are given in the units of Fe atomic volume evaluated by relaxing a ferromagnetic bcc unit cell using the respective exchange correlation functionals.

Similarly, the atomic magnetism of some 3d transition metals likely contributes to the anomalous relaxation volumes of their solutes in tungsten. In this section, we explore this magneto-volume effect.

Electrons in transition metal elements from the 3d series may fill the e_g and t_{2g} bands asymmetrically to form local magnetic moments when substituted into a different host lattice [112]. Iron-based alloys exhibit a myriad of complex magnetic states, such as ferromagnetic, ferrimagnetic, antiferromagnetic [9], incommensurate spin density waves [65–67], and spin glasses [113,114]. Their mechanical properties are partially governed by the population of these magnetic states [115,116]. For example, in pure iron, the softening of the tetragonal shear modulus C' above the Curie temperature T_C and the associated transformation of dislocation structures are driven by the phase instability driven by thermal magnetic and atomic vibrational fluctuations [117–120]. The high temperature fcc crystal phase of iron owes its stability to the free energy contributions arising from both lattice phonon and magnetic excitations [97,104,121–124].

Magnetism is also responsible for the $\langle 110 \rangle$ dumbbell being the most stable SIA configuration in α -Fe, different from the defect structure found in other bcc metals [24,26]. Magnetic interactions lower the energy of each interstitial configuration. However, non-Heisenberg magnetic interactions in the $\langle 111 \rangle$ configuration add an energy penalty which results in the $\langle 110 \rangle$ and tetrahedral configurations having lower energy than the $\langle 111 \rangle$ dumbbell and crowdion [125]. Magnetic moments of atoms change significantly in the vicinity of dislocations and defects [126,127].

To investigate the effect of magnetism on the relaxation volume of solute atoms, we performed constrained DFT calculations [107]. Since constrained DFT calculations are computationally demanding, simulations were performed using smaller simulation cells. We used simulation cells containing 54 atoms ($3 \times 3 \times 3$ unit cells) and a $5 \times 5 \times 5$ k-point mesh. The system size remains large enough for solutes to be considered isolated. The solute concentration is now 1.85%.

We constrain the magnitude of magnetic moments of solutes $|\mathbf{M}_I|$ to various values. They vary from 3 to $-3 \mu_B$ with a step of $0.3 \mu_B$. The minus sign means that the magnetic moment of a 3d transition metal solute atom points in the opposite direction to the moments of the host iron atoms. In the ferromagnetic bcc iron matrix, the magnetic moment of a solute atom is aligned collinearly with the magnetic moments of iron atoms. Noncollinearity is not considered in this study. The method is applied to all the 3d transition metal series elements substituted into both Fe and W.

In Figs. 9 and 10, we plotted the energy and relaxation volume against the magnitude of the magnetic moment of a solute in tungsten and iron, respectively. Energies are minimum when the magnitude of the magnetic moment attains the same value as in the unconstrained case (Tables V and IV). This also confirms that there is no spurious contribution from the penalty energy E_p , which converges to a sufficiently small value if λ is large [107].

In bcc tungsten, the energy of Mn, Fe, or Co solutes is minimum if the solute atom has a finite magnetic moment. These solutes have stable magnetic configurations. The spontaneous

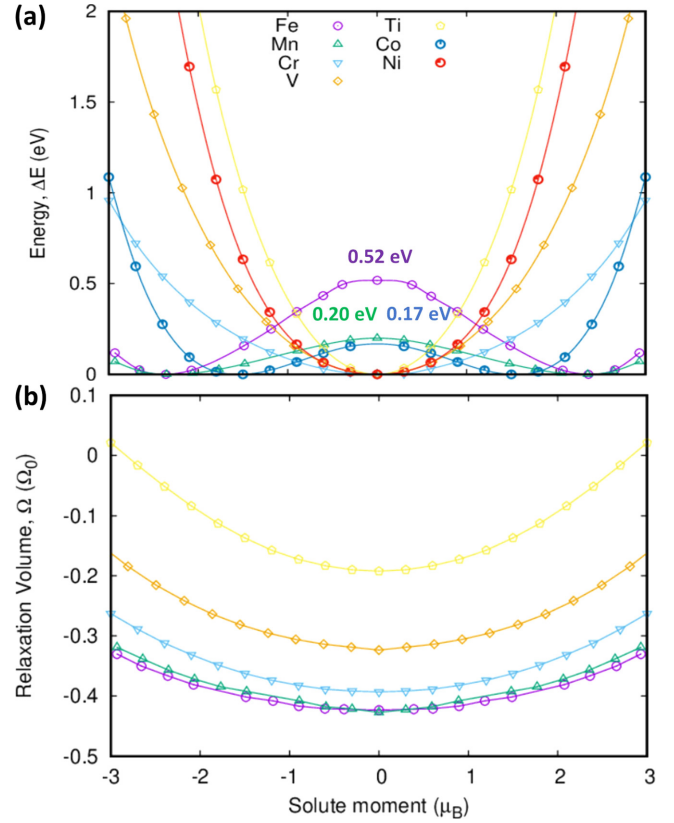


FIG. 9. Relative energy and relaxation volumes for dilute 3d transition metal series substitutions in bcc tungsten. Mn_W , Fe_W , and Co_W maintain spontaneous magnetic moments of 2.32, 2.38, and $1.56 \mu_B$, with the collinear spin-flip switching barriers of 0.20, 0.52, and 0.17 eV, respectively. The relative total energy is $\Delta E = E - E_0$, where E_0 is the energy of the most stable magnetic configuration obtained within the constrained DFT calculations.

atomic magnetic moment of a Fe_W impurity at a substitutional site is $2.38 \mu_B$, which is greater than the atomic magnetic moment in bulk bcc Fe, where it equals $2.2 \mu_B$. The lattice parameter of W is larger than that of Fe, causing the substitutional Fe_W atom to be under effective tensile strain. Bulk strain-magnetization curves show that the atomic magnetic moment of ferromagnetic bcc Fe increases as a function of its lattice parameter [125].

The magnetic moments of Mn_W and Co_W substitutional atoms are 2.32 and $1.56 \mu_B$, respectively. The magnetic moment of Mn increases relative to the bulk value of $0.87 \mu_B$, whereas for Co it decreases from its elemental value of $1.76 \mu_B$. Co is a strong ferromagnet, but when Co is substituted into a lower valence W lattice, its electrons are depleted from the majority band. The large increase in the magnetic moment of Mn_W arises from the inherent magnetic ordering in elemental Mn, where magnetism is known to contribute to the bewildering structural complexities of its allotropes. In its bcc phase (δ phase), Mn is ferromagnetic [128] and evolves from a low to high spin configuration under hydrostatic strain, as illustrated in Fig. 11.

Relaxation volume curves for Ni_W are not shown because the computed energy values did not converge satisfactorily to enable accurate stress calculations. The energy curves are

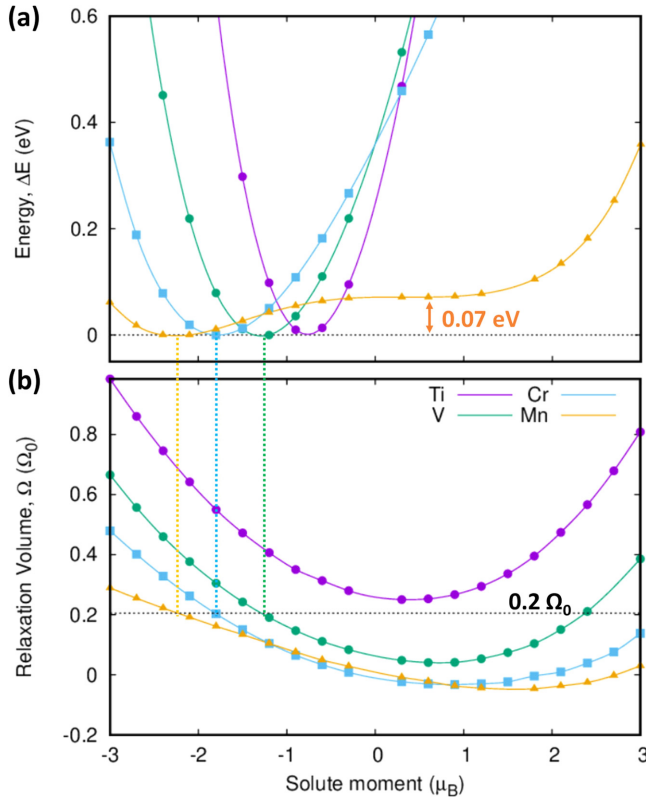


FIG. 10. Identification of a magnetovolume effect from the relative energy and relaxation volumes for 3d transition metal substitutions in bcc Fe. The relaxation volumes of Ti_{Fe} , V_{Fe} , and Cr_{Fe} at the energy minima are very close to $\Omega^{\text{rel}} \approx 0.2 \Omega_0$. The relative total energy is defined as $\Delta E = E - E_0$, where E_0 is the energy of the most stable magnetic configuration obtained using constrained DFT calculations [107].

still provided since the errors in DFT energies are of second order in uncertainties, whereas stresses are accurate only to first order.

The energy barriers for collinear reversal of the solute magnetic moment is calculated to be 0.52, 0.20, and 0.17 eV for Fe_W , Mn_W , and Co_W . The collinear spin-flip switching barrier for Fe_W in a 250-atom cell is calculated to be 0.49 eV. The absolute value of Ω^{rel} is found to vary in the 5–10% range in comparison with values obtained using smaller simulation cells. This illustrates the origin of a slight discrepancy, arising from the finite cell size effects, between the values given in Figs. 9 and 10 and values given in Figs. 5 and 6.

Relaxation volumes for solutes in W are minimum when there is no magnetic moment on a solute atom. Therefore, the energy required to increase the size of a solute in W is less than that necessary for the symmetry-breaking-mediated formation of a local magnetic moment at Mn_W , Fe_W , and Co_W substitutional solutes. This is an important consideration in the context of mesoscale alloy models, which often focus on continuum approximations and linear elasticity argument, neglecting the local electronic structure effects.

The relative sizes of solutes in W are in qualitative agreement with the analysis of changes in grain boundary cohesion due to impurities [34]. Scheiber *et al.* [34] identified that Cr_W , Mn_W , Fe_W , and Co_W , which we find to be the most undersized

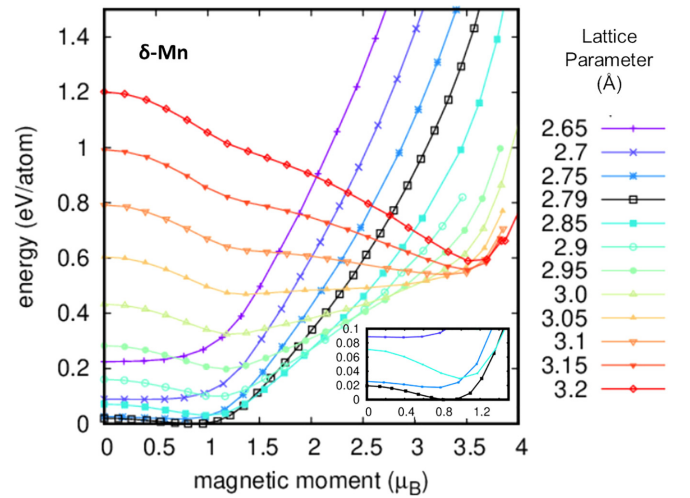


FIG. 11. Energy-magnetic moment hypersurface for different lattice parameters of ferromagnetic bcc $\delta\text{-Mn}$. Calculations performed using the constrained DFT method for a two-atom simulation cell, using collinear magnetic moments, with a 300 eV cutoff and a $16 \times 16 \times 16$ gamma-centered k-point grid. Energies are referenced relative to the lowest energy of $\delta\text{-Mn}$, which corresponds to the lattice parameter of 2.79 Å (black) [69,94], with the corresponding magnetic moment of $0.87 \mu_B$. Under tensile hydrostatic strain, $\delta\text{-Mn}$ transforms from a low-spin to a high-spin ferromagnetic configuration.

elements, can strengthen grain boundaries. At the same time, oversized solutes were found to promote embrittlement. Recent experimental observations noted the propensity of Fe_W to have an anomalously strong binding energy at grain boundaries [129] and at dislocation loops. Our analysis is consistent with these experimental observations. In the vicinity of defects characterized by large local stress fields, Fe_W can quench its magnetic moment and reduce its volume to more compactly fill the available space and minimize the pressure it exerts on its neighbors. In the absence of other chemical effects, we would also expect Co_W and Mn_W to strongly bind to defects while being barely soluble in a crystalline bulk material.

For transition metal solutes in bcc iron, the spontaneous magnetic moments derived from the present study are consistent with experimental observations [7,130–139] and with the Slater-Pauling curve [140,141]. That is, for substitutions of an element from a lower group number, where the number of electrons per atom (e/a) is less than approximately 8, the number of minority electrons remains fixed and electrons are added to the majority band, increasing the magnetic moment as the e/a value approaches 8. Once the majority band is full, the minority band becomes increasingly populated, decreasing the magnetic moment.

For the case of Mn_{Fe} illustrated in Fig. 10, we recover the same complex energy curve as that discovered in Ref. [94]. The energy is minimized when the magnetic moment of Mn_{Fe} is antiparallel to Fe with a magnitude of $-2.2 \mu_B$ and with a 0.07 eV energy barrier for its reorientation into a parallel alignment. From Fig. 11, elemental Mn in its bcc phase exhibits a flattening of the energy-magnetic moment hypersurface under small tensile hydrostatic strains. We infer that when

Mn is substituted into bcc Fe, which has a larger lattice parameter than Mn, this flattening of the magnetic hypersurface is retained. Small localized strains can promote ferromagnetic alignment with neighboring Fe atoms, also often noted in experimental studies [128].

A peculiar consequence of the Mn_{Fe} magnetovolume relationship is that even small changes in energy, or small applied magnetic fields, can significantly change its effective volume. Further investigation is necessary to understand the consequences of this observation for Mn-doped steels in high magnetic field environments, such as plasma-facing components. This is required to determine whether Mn could beneficially contribute to the reduction of the ductile-to-brittle transition temperature in operational environment by reducing hardness due to the apparent smaller sizes of Mn solutes.

The relaxation volumes of V_{Fe} , Cr_{Fe} , and Mn_{Fe} are approximately 20% of the host atom (i.e., $0.2\Omega_0$). The solute acquires a magnetic moment, with the orientation being antiferromagnetic to that of the host lattice. As the magnitude of the magnetic moment is reduced by the constraining field, the relaxation volume decreases, exhibiting a pronounced magneto-volume effect. If the magnetic moments of solutes are suppressed artificially, the relaxation volumes decrease. The volumes of solute atoms become similar to that of an iron atom, as one would expect from their metallic radii. Therefore, the observed anomalously large volumes of $3d$ transition metal solutes in bcc iron can be attributed to the enhanced magnetic moments induced in these elements. However, unlike in W, which is nonmagnetic, the relaxation volumes are not at a minimum if the solute atom magnetic moment vanishes. This is due to the effective magnetic field acting on the solute from the neighboring magnetic iron atoms.

The magnetovolume effect has been previously identified as being lower in high-entropy Fe-Cr-Ni-Mn alloys [69] (HEA) than in Fe-Cr-Ni alloys [142], which might explain why HEAs exhibit reduced swelling under radiation exposure compared to conventional steels. Our work provides a quantitative insight into how magnetic properties can affect short-range order, as recently predicted in medium and high-entropy alloys [40].

Both experimental observations and DFT calculations show that the bulk bcc Cr and bcc Fe have similar lattice parameters ($a_{\text{Fe}}^{\text{exp}} = 2.86 \text{ \AA}$, $a_{\text{Cr}}^{\text{exp}} = 2.89 \text{ \AA}$) and similar metallic radii (Fig. 6). Nonetheless, nanoindentation and TEM investigations of ion-irradiated samples of nominally concentrated FeCr alloys show that the presence of Cr_{Fe} increases the retention of defects. This results in notable irradiation hardening [143]. The effect is known to increase with Cr concentration. This is observed in alloys with concentrations as low as 2.5–5% [6,109,143], where the enthalpy of formation is negative, implying that precipitation is unfavorable under nonirradiated steady-state conditions. The anomalous oversizing of dilute Cr atoms found in this and earlier work [73] might need to be taken into account in microstructure evolution calculations to understand why chemically similar iron Cr atoms appear to promote defect retention and defect pinning even at low concentrations.

The variation of the Co_{Fe} and Ni_{Fe} relaxation volumes as a function of the magnetic moment are not shown in Fig. 10(b) because we were unable to compute the con-

verged stress values using the constrained DFT method. This is not unexpected, considering that bulk Co and Ni are both strong ferromagnets. This makes changing the electron density difficult by applying a magnetic constraint. This applies in particular to the case of Fe host matrix, where the majority spin d band of neighboring atoms is nearly fully populated.

Although the spontaneous magnetic moments of $4d$ and $5d$ transition metal series elements are much smaller than those of $3d$ elements in their substitutional solute form in Fe, we observe the same qualitative effects. Suppressing the magnetic moment using a constraint field significantly reduces the relaxation volume to a value comparable to the relative volume estimate. For example, the relaxation volume of Mo_{Fe} is $0.6\Omega_0$ with a spontaneous magnetic moment of $-0.82 \mu_B$. When the relaxation volume is minimized using the constraint field producing a magnetic moment of $+0.5 \mu_B$, the relaxation volume of $0.42\Omega_0$ becomes comparable to the relative volume of $0.34V_W^{\text{met}}$.

In constrained noncollinear DFT calculations, the concepts of spin-up and spin-down magnetic states are ill-defined. However, the LDOS can still be calculated from the magnetization density [106]. In each case, there is a pseudogap minimum in the LDOS at the Fermi energy, which stabilizes the spontaneous magnetic moment of each solute in Fe as illustrated for V_{Fe} , Cr_{Fe} and Mn_{Fe} in Fig. 12. The pseudogap minimum stabilizes and pins the position of the Fermi energy, making it more difficult for electrons to be excited from one band to another [144]. For the naturally magnetic metal solutes (e.g. Cr or Mn), the moments minimizing the relaxation volumes correspond to the Fermi energies situated at the maxima of the LDOS.

C. Insights from electronic structure analysis

We can gain some insight into the formation of magnetic moments in solutes by analyzing their density of states. We limit current analysis to collinear configurations only, where spin-up and spin-down states are well-defined. We examine the electronic structure of magnetic solutes computed using 250-atom simulation cells that do not involve magnetic constraints.

One can determine how many electrons with a given spin $\alpha = \uparrow, \downarrow$ are in each valence band at atomic site i by integrating all the occupied states in band (β) from the projected LDOS $D_{i,\beta}^{\alpha}$:

$$n_{i,\beta}^{\alpha} = \int_{-\infty}^{\varepsilon_F} D_{i,\beta}^{\alpha}(\varepsilon) d\varepsilon, \quad (14)$$

where ε_F is the Fermi energy. The magnetic moment of an atom is equal to the difference between the number of spin-up and spin-down electrons:

$$m_i = n_i^{\uparrow} - n_i^{\downarrow}, \quad (15)$$

where $n_i^{\alpha} = \sum_{\beta} n_{i,\beta}^{\alpha}$.

The site-resolved spin-polarized band energy is equal to the first moment of the LDOS:

$$E_i^{\text{spin band}} = \sum_{\alpha} \int_{-\infty}^{\varepsilon_F} \varepsilon D_i^{\alpha}(\varepsilon) d\varepsilon. \quad (16)$$

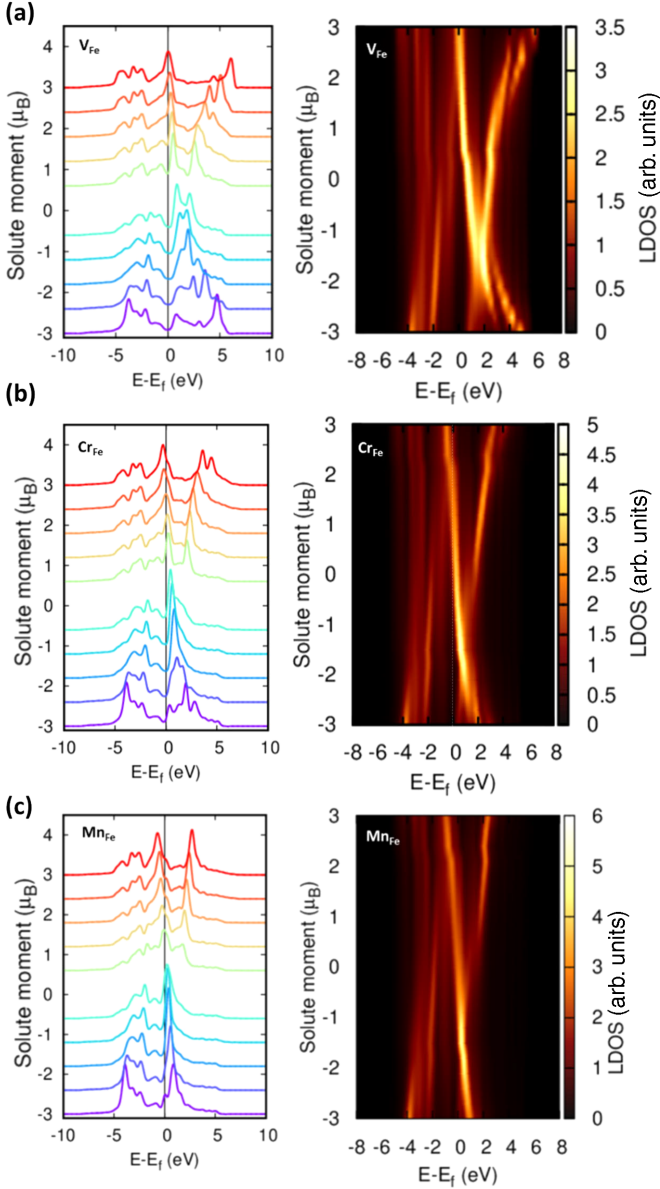


FIG. 12. Local density of states (LDOS) of (a) V_{Fe} , (b) Cr_{Fe} , and (c) Mn_{Fe} . They develop spontaneous magnetic moments of -1.40 , -1.83 , and $-2.13 \mu_B$, respectively. Left panels show the LDOS as a function of solute metals constrained magnetic moment. Right panels present maps of the sum of d -electron contributions to the LDOS.

If we consider two magnetic configurations labeled (1) and (2), their band energy difference can be written as

$$\Delta E_{(2)-(1)}^{\text{spin band}} = \sum_{\alpha} \int_{-\infty}^{\epsilon_F} \epsilon (D_{(2)}^{\alpha}(\epsilon) - D_{(1)}^{\alpha}(\epsilon)) d\epsilon. \quad (17)$$

To write it explicitly:

$$\Delta E_{(2)-(1)}^{\text{spin band}} = \int_{-\infty}^{\epsilon_F} (\epsilon D_{(2)}^{\uparrow}(\epsilon) + \epsilon D_{(2)}^{\downarrow}(\epsilon)) d\epsilon - \int_{-\infty}^{\epsilon_F} (\epsilon D_{(1)}^{\uparrow}(\epsilon) + \epsilon D_{(1)}^{\downarrow}(\epsilon)) d\epsilon. \quad (18)$$

However, the magnetic energy difference between (1) and (2) cannot be directly determined from band energy

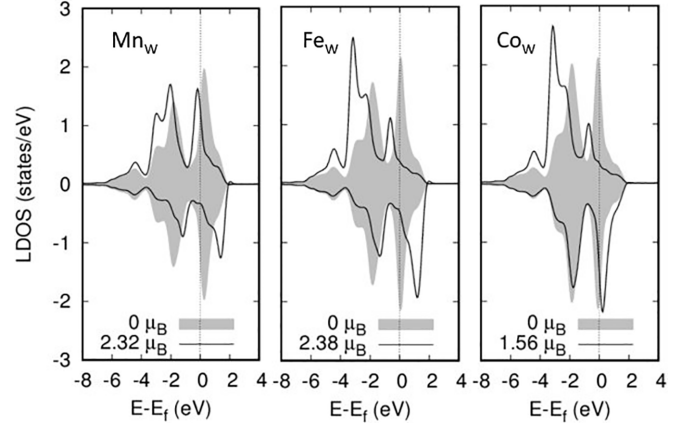


FIG. 13. LDOS of Mn, Fe, and Co substitutional solutes in W of both metastable nonmagnetic and spontaneous magnetic configurations are shown. The rigid band approximation does not apply to magnetic solutes.

differences alone, as these do not represent the total energy difference between magnetic configurations [145]. Instead, we can employ the Stoner model of magnetism [110,146] and the Rigid Band Approximation (RBA) [46]. Knowing that the contribution of band splitting to the on-site energy is $\pm I_i m_i$, the analysis can be simplified using an effective Stoner parameter I_i^{eff} , defined as the on-site exchange splitting between the spin-up and spin-down electrons in a configuration i necessary to produce the average magnetic moment $\langle m \rangle_i$.

Within the RBA framework, we can find the effective Stoner parameter I_i^{eff} by starting from a nonmagnetic system. It relates the shifting of the spin-up and spin-down Fermi energies to the creation of magnetism. The relationship can be written as

$$I_i^{\text{eff}} \langle m \rangle_i = \epsilon_{F,NM(i)}^{\uparrow} - \epsilon_{F,NM(i)}^{\downarrow}. \quad (19)$$

Once we know the effective Stoner parameter, we can calculate the magnetic energy contribution using the Stoner model:

$$E_{\text{Stoner-RBA}} = \frac{1}{4N} \sum_j I_j m_j^2 \approx \frac{1}{4} I_i^{\text{eff}} \langle m \rangle_i^2, \quad (20)$$

where factor $1/4$ comes from the double-counting correction, see, e.g., Appendix A in Ref. [126].

Performing electronic structure analysis is challenging in the current work due to the strong spatial heterogeneity of our systems. Unlike conventional treatments, where bands are constructed from fully extended states delocalized over the entire cell, current cases involve a magnetic impurity situated at the center of a cell host atoms. As a result, the RBA and conventional Stoner model may not be directly applicable. Instead, using an effective Stoner parameter is necessary in the analysis, since the total DOS satisfies the RBA whereas the LDOS of a magnetic solute does not (Fig. 13). After considering the double counting contributions [145], the change in magnetic energy is [46]

$$\Delta E_{(2)-(1)}^{\text{mag}} = \Delta E_{(2)-(1)}^{\text{spin band}} + \frac{1}{4} (I_{(2)}^{\text{eff}} \langle m \rangle_{(2)}^2 - I_{(1)}^{\text{eff}} \langle m \rangle_{(1)}^2). \quad (21)$$

Considering tungsten as the host lattice, as it is non-magnetic, $\langle m \rangle_{(\text{NM})} = 0$. If Fe_W is the substitutional solute, which has the largest spontaneous magnetic moment among all magnetic solutes, for a 250-atom simulation cell, $\langle m \rangle \approx 1 \times 10^{-2} \mu_B$, such that $\langle m \rangle^2 \approx 1 \times 10^{-4} \mu_B^2$. Considering that for pure Fe [110,146,147], $I \approx 1 \text{ eV } \mu_B^{-1}$, the magnitude of the Stoner contribution is of the order:

$$I_{(\text{FM})}^{\text{eff}} \langle m \rangle_{(\text{FM})}^2 - I_{(\text{NM})}^{\text{eff}} \langle m \rangle_{(\text{NM})}^2 \approx 1 \times 10^{-4} \text{ eV}, \quad (22)$$

which is much smaller than 1 eV.

We summarize the site-resolved number of electrons and changes in the band energy in Table VI. The $\Delta E_{(2)-(1)}^{\text{spin band}}$ contribution is 2–4 orders of magnitude larger than the Stoner term. Furthermore, the error in the spin-band energy calculations is of order 10^{-2} eV , so we may safely make the approximation that $\Delta E_{(2)-(1)}^{\text{mag}} \approx \Delta E_{(2)-(1)}^{\text{spin band}}$ for the W lattice.

We note that the magnetization defined in Eq. (10) is calculated in the nonoverlapping PAW spheres, and so is the projection scheme for the density of states. As such, the sum of the atom-centered charges calculated for each atom is not exactly equal to the total number of valence electrons (Table I).

In the d -block transition metals, the dominant contribution to the magnetic moment of a solute atom arises from the exchange splitting of energy levels of the spatially localized d electrons centered on the solute. The majority of chemical changes also occurs in the d electrons, with only minor changes in hybridization effects associated with the outer spatially delocalized s electrons. Energies of the s and p spin bands vary by less than 10% between the magnetic and non-magnetic solute configurations, while the d band states change significantly.

Properties of $3d$ solute substitutions in W are presented in Table VI. The change in the total spin-band energy, and therefore magnetic energy, decreases as a function of group number. A similar trend is observed for the $3d$ solute substitutions in Fe, as shown in Table VII. The Stoner contribution is also negligible, as the exchange splitting between configurations is comparable, and the difference is much smaller than the changes in band energy. This is because $m_{\text{av}}^{(2)} \approx m_{\text{av}}^{(1)}$, where configurations (1) and (2) refer to the solute in its spontaneous magnetic moment and its metastable nonmagnetic state, respectively. The magnetic energy for Co_W strongly favors stability, whereas the magnetic contribution is unfavorable for Mn_W .

Other energy contributions ($\Delta E - \Delta E_{\text{mag}}$), predominantly elastic energy, must therefore increase with group number to account for the total energy curves ($\Delta E = E - E_0$) shown in Fig. 9. This is expected, as elastic energy tends to increase with group number due to the additional electrons provided by the solute atoms, which exert positive pressure on neighboring atoms.

D. Role of neighboring atoms

A solute atom usually has a different valence in comparison to atoms in the host metal, and, as a result, electrons are transferred between the solute atom and its neighbors. Therefore, the electronic structure of the host metal in the vicinity of a solute changes relative to the bulk, and these changes need to

be taken into account for a comprehensive description of the volume relaxation effect.

The occurrence of relaxation volume reflects the distribution of stress in a constrained simulation cell, evaluated as a sum of local stress tensors, accounting for each volume element in the cell. As such, the overall value of the relaxation volume also accounts for the contributions from the host atoms neighboring the solute. The electronic energy decomposition shows that neighboring atom contributions are indeed required to understand the full effects of structural relaxation. Likewise, the anomalous size of a solute atom is also a consequence of the variation of the electronic structure in its close neighborhood. Volume relaxation is not an elastic effect but rather an electronic effect. In other words, it is a chemical phenomenon resulting from the perturbation of electronic states in the vicinity of a solute, not dissimilar to that occurring in the vicinity of a self-interstitial atom defect [28].

In Fig. 14, the changes in the occupancy of s , p , and d states are shown for the first-, second-, and third-NNs to the substitutional solutes from the $3d$ series. For both W and Fe host lattices, the number of electrons on the third-NN atoms has already become bulklike, indicating that only the changes to the first- and second-NN atoms require attention. The changes in the electron occupation of neighboring atoms for Mn_W , Fe_W , and Co_W are also shown in Fig. 14 in solid symbols for their nonmagnetic states. However, since the changes in the electron occupancy between the magnetic and nonmagnetic cases are similar, this indicates that the magneto-volume effect explored in Sec. III B represents a dominant contribution to the anomalous size effects for these transition metals in tungsten.

In the tungsten lattice, we observe a reduction in the occupancy of s , p , and d electrons of the first-NN atoms of the $3d$ transition metal substitutions. If we consider that a small decrease in the occupancy of the orbitals results in a minor change in the screening of the nuclear charge, and electron-electron repulsion dominates, we can infer that the size of the atom will decrease. In the bcc structure, there are eight first-NN atoms. A small reduction in their volumes will each provide a negative contribution to the relaxation volume. Combined with the magneto-volume effect, this explains why the $3d$ series elements appear anomalously small in tungsten (Fig. 5) as their first NNs shrink.

To confirm this interpretation, we performed a Bader analysis which partitions the supercell volume using isosurfaces characterized by zero net flux in the gradient vector field of the charge density. The volume enclosed by the zero flux surface is the Bader volume of an atom. The total charge density within the Bader volume is the Bader charge. We used the BADER CHARGE ANALYSIS code [148] to perform this decomposition. Care was taken to ensure that the core charges, often omitted in pseudopotentials, were included in the valence charge before the Bader analysis.

We present the relative Bader charge Δq^{Bader} , defined as the charge calculated from the Bader charge analysis less the valence of the atom (where the valencies of the PAW pseudopotentials used are given in Table I), and the Bader volume in Tables VIII and IX. For comparison, we also provide the change in the charge calculated using the DOS.

TABLE VI. Properties of $3d$ solute substitutions in bcc W, computed for their lower energy magnetic states and higher energy nonmagnetic metastable states (denoted by the NM superscript). n_β^α is the number of valence electrons with angular momenta β and spin α . The total magnetization M is the difference between spin-up and spin-down total occupancies $\sum_{\alpha,\beta} n_\beta^\alpha$. E_β^α are the spin-band energies of β electrons with spin α at the substitutional atomic site (in eV). $E_i^{\text{spin band}}$ is the sum of E_β^α contributions (in eV). E_β^α is the spin-band energy of the total simulation cell containing the specific solute (in eV). ID defines a label for each simulation. Rows with atom/site labeled (a) and (b) are the differences between configurations with ID (a) and (b).

ID	Atom/site	$n_s^\uparrow$	$n_s^\downarrow$	$n_p^\uparrow$	$n_p^\downarrow$	$n_d^\uparrow$	$n_d^\downarrow$	M	$E_s^\uparrow$	$E_s^\downarrow$	$E_p^\uparrow$	$E_p^\downarrow$	$E_d^\uparrow$	$E_d^\downarrow$	$E_i^{\text{spin band}}$	$E_{(J)}^{\text{spin band}}$
Host																
(7)	W	0.34	0.34	0.36	0.36	2.07	2.07	0.00	-1.95	-1.95	-1.06	-1.06	-6.43	-6.43	-18.85	-5135.87
Solute																
Solute with multiple stable collinear magnetic states																
(2)	Mn _W	0.18	0.16	0.21	0.19	3.64	1.37	2.32	-0.90	-0.80	-0.59	-0.54	-7.54	-2.41	-12.78	-5114.23
(1)	Mn _W ^{NM}	0.17	0.17	0.20	0.20	2.50	2.50	0.00	-0.87	-0.87	-0.59	-0.59	-5.06	-5.06	-13.05	-5123.78
	(2) - (1)	0.01	-0.01	0.01	-0.01	1.14	-1.13	2.32	-0.03	0.03	0.00	0.05	-2.48	2.65	+0.27	9.55
(4)	Fe _W	0.22	0.21	0.27	0.25	4.26	1.90	2.38	-1.17	-1.07	-0.78	-0.74	-10.98	-3.43	-18.17	-5118.74
(3)	Fe _W ^{NM}	0.21	0.21	0.25	0.25	3.10	3.10	0.00	-1.09	-1.09	-0.75	-0.75	-5.71	-5.71	-15.10	-5118.99
	(4) - (3)	0.01	0.00	0.02	0.00	1.16	-1.20	2.38	-0.08	0.02	-0.03	0.01	-5.27	-9.14	-3.07	0.25
(6)	Co _W	0.22	0.21	0.25	0.25	4.37	2.81	1.57	-1.15	-1.11	-0.74	-0.72	-11.34	-5.16	-20.21	-5120.14
(5)	Co _W ^{NM}	0.21	0.21	0.24	0.24	3.62	3.62	0.00	-1.08	-1.08	-0.70	-0.70	-6.26	-6.26	-16.10	-5113.83
	(6) - (5)	0.01	0.00	0.01	-0.01	0.75	-0.81	1.57	-0.07	-0.03	-0.04	-0.02	-5.08	1.10	-4.11	-6.31
Tungsten atoms neighboring magnetic solutes																
(9)	W _{INN-Mn}	0.33	0.34	0.35	0.35	2.05	2.07	-0.02	-1.89	-1.89	-1.00	-1.00	-6.08	-6.16	-18.02	
(8)	W _{INN-Mn} ^{NM}	0.34	0.34	0.36	0.36	2.06	2.06	0.00	-1.92	-1.92	-1.03	-1.03	-6.30	-6.30	-18.48	
	(9) - (8)	-0.01	0.00	-0.01	-0.01	-0.01	0.01	-0.02	0.03	0.03	0.03	0.03	0.22	0.14	0.46	
	(9) - (7)	-0.01	0.00	-0.01	-0.01	-0.02	0.00	-0.02	0.06	0.06	0.06	0.06	0.35	0.27	0.83	
	(8) - (7)	0.00	0.00	0.00	0.00	-0.01	-0.01	0.00	0.03	0.03	0.03	0.03	0.13	0.13	0.37	
(12)	W _{INN-Fe}	0.33	0.34	0.35	0.35	2.07	2.05	0.02	-1.89	-1.89	-1.01	-1.00	-6.11	-6.13	-18.03	
(11)	W _{INN-Fe} ^{NM}	0.34	0.34	0.36	0.36	2.06	2.06	0.00	-1.91	-1.91	-1.02	-1.02	-6.22	-6.22	-18.29	
	(12) - (11)	-0.01	0.00	-0.01	-0.01	0.01	-0.01	0.02	0.02	0.02	0.01	0.02	0.11	0.09	0.26	
	(12) - (7)	-0.01	0.00	-0.01	-0.01	0.00	-0.02	0.02	0.06	0.06	0.05	0.06	0.32	0.30	0.82	
	(11) - (7)	0.00	0.00	0.00	0.00	-0.01	-0.01	0.00	0.04	0.04	0.04	0.04	0.21	0.21	0.56	
(14)	W _{INN-Co}	0.34	0.33	0.35	0.35	2.09	2.03	0.06	-1.90	-1.89	-1.01	-1.00	-6.16	-6.11	-18.07	
(13)	W _{INN-Co} ^{NM}	0.34	0.34	0.35	0.35	2.06	2.06	0.00	-1.89	-1.89	-1.00	-1.00	-6.12	-6.12	-18.04	
	(14) - (13)	0.00	-0.01	0.00	0.00	0.03	-0.03	0.06	-0.01	0.00	-0.01	0.00	-0.04	0.01	-0.03	
	(14) - (7)	0.00	-0.01	-0.01	-0.01	0.02	-0.04	0.06	0.05	0.06	0.05	0.06	0.27	0.32	0.78	
	(13) - (7)	0.00	0.00	-0.01	-0.01	-0.01	-0.01	0.00	0.06	0.06	0.06	0.06	0.31	0.31	0.81	
Solute																
	Fe _W	0.27	0.27	0.41	0.41	1.30	1.30	0.00	-1.23	-1.23	-1.06	-1.06	-2.68	-2.68	-9.95	
	V _W	0.26	0.26	0.37	0.37	1.75	1.75	0.00	-1.24	-1.24	-1.05	-1.05	-3.66	-3.66	-11.90	
	Cr _W	0.23	0.23	0.32	0.32	2.15	2.15	0.00	-1.17	-1.17	-0.94	-0.94	-4.61	-4.61	-13.43	
	Ni _W	0.22	0.22	0.25	0.25	4.15	4.15	0.00	-1.17	-1.17	-0.72	-0.72	-7.70	-7.70	-19.17	
Neighbors																
	W _{INN-Ti}	0.34	0.34	0.35	0.35	2.07	2.07	-0.00	-1.87	-1.87	-0.97	-0.97	-6.04	-6.04	-17.76	
	W _{INN-V}	0.34	0.34	0.36	0.36	2.07	2.07	-0.00	-1.90	-1.90	-1.00	-1.00	-6.16	-6.16	-18.12	
	W _{INN-Cr}	0.34	0.34	0.36	0.36	2.06	2.06	-0.00	-1.92	-1.92	-1.02	-1.02	-6.27	-6.27	-18.42	
	W _{INN-Ni}	0.33	0.33	0.35	0.35	2.06	2.06	-0.00	-1.87	-1.87	-0.99	-0.99	-6.03	-6.03	-17.78	

Voronoi tessellation [149] is another spatial partitioning method. The domain defined by a supercell is partitioned into many Voronoi volumes. Each volume is assigned to the closest atom such that the faces of each Voronoi cell are equidistant to two or more atoms. For this decomposition, we use Voro + +

[150] with the results given in Tables X and XI. Although the volumes attributed to the first- and second-NN host atoms differ between the Voronoi and Bader methods, there is general agreement as to whether the volumes have increased or decreased relative to their volume in the pristine crystal.

TABLE VII. Spin-decomposed properties of 3d solute substitutional atoms and their first-nearest neighbors in bcc Fe. n_β^α is the number of valence electrons with angular momenta β and spin α projected onto an atomic site. The total magnetization M_i is the difference between the spin-up and spin-down site occupancies $\sum_{\alpha,\beta} n_\beta^\alpha$. E_β^α are the spin-band energies of β electrons with spin α at the atomic site (in eV). $E_i^{\text{spin band}}$ is the sum of the E_β^α contributions (in eV).

Atom/site	$n_s^\uparrow$	$n_s^\downarrow$	$n_p^\uparrow$	$n_p^\downarrow$	$n_d^\uparrow$	$n_d^\downarrow$	M_i	$E_s^\uparrow$	$E_s^\downarrow$	$E_p^\uparrow$	$E_p^\downarrow$	$E_d^\uparrow$	$E_d^\downarrow$	$E_i^{\text{spin band}}$
Host														
Fe	0.24	0.25	0.24	0.30	4.24	1.99	2.18	-1.16	-1.13	-0.75	-0.65	-8.92	-3.13	-15.74
Solute														
Ti _{Fe}	0.28	0.33	0.35	0.49	0.94	1.71	-0.96	-1.19	-1.31	-0.99	-0.95	-2.40	-3.12	-9.96
V _{Fe}	0.27	0.32	0.33	0.45	1.14	2.38	-1.41	-1.22	-1.38	-1.01	-0.97	-2.89	-5.05	-12.53
Cr _{Fe}	0.24	0.29	0.29	0.40	1.32	2.98	-1.83	-1.16	-1.34	-0.91	-0.91	-3.18	-7.43	-14.93
Mn _{Fe}	0.18	0.22	0.18	0.26	1.45	3.51	-2.18	-0.88	-1.05	-0.59	-0.60	-3.15	-9.76	-16.03
Co _{Fe}	0.24	0.26	0.23	0.30	4.50	2.72	1.69	-1.20	-1.21	-0.74	-0.67	-11.24	-5.03	-20.09
Ni _{Fe}	0.25	0.28	0.24	0.32	4.61	3.63	0.87	-1.28	-1.35	-0.77	-0.71	-12.33	-8.24	-24.69
Neighbor														
Fe _{1NN-Ti}	0.24	0.25	0.24	0.30	4.22	2.05	2.10	-1.15	-1.12	-0.72	-0.64	-8.77	-3.20	-15.59
Fe _{1NN-V}	0.24	0.25	0.24	0.30	4.23	2.02	2.14	-1.17	-1.14	-0.74	-0.66	-9.11	-3.29	-16.12
Fe _{1NN-Cr}	0.24	0.25	0.25	0.30	4.25	2.00	2.19	-1.18	-1.15	-0.76	-0.68	-9.43	-3.34	-16.54
Fe _{1NN-Mn}	0.24	0.25	0.25	0.30	4.24	1.99	2.19	-1.19	-1.16	-0.77	-0.69	-9.48	-3.33	-16.61
Fe _{1NN-Co}	0.24	0.25	0.24	0.30	4.30	1.92	2.30	-1.17	-1.13	-0.76	-0.66	-9.32	-3.07	-16.10
Fe _{1NN-Ni}	0.24	0.25	0.24	0.29	4.32	1.90	2.36	-1.17	-1.13	-0.76	-0.66	-9.55	-3.04	-16.31

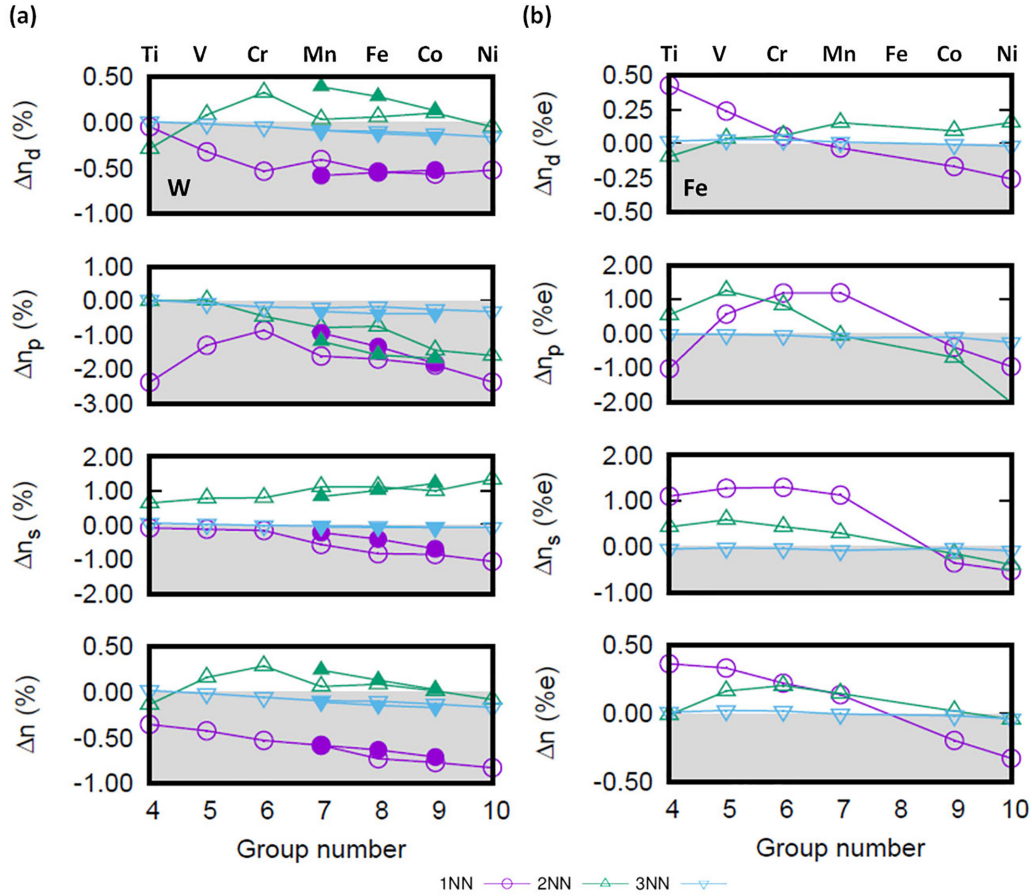


FIG. 14. Change in the number of electrons $n_{i,\beta} = n_{i,\beta}^\uparrow + n_{i,\beta}^\downarrow$ occupying the $\beta = s, p$, and d bands of atoms i located in first- (purple circles), second- (green triangles), and third- (blue inverted triangles) nearest-neighbor sites, relative to different 3d transition metal substitutions in bcc (a) W and (b) Fe. Results are presented in units percentage change from their bulk value (%). For W, solid symbols show the change for the metastable nonmagnetic configurations of Mn_W, Fe_W, and Co_W.

TABLE VIII. Charge difference (Δq^{Bader}) and Bader volumes (V^{Bader}) of transition metals and their first- and second-nearest neighbors when substituted into bcc Fe according to the Bader analysis. Charge differences computed using the density of states (Δq^{DOS}) are provided for comparison. Differences in the Bader charge are relative to the number of valence electrons (see Table I). Differences in the DOS charges of iron atoms neighboring the solute are relative to its value in perfect bulk (7.273e) using an RWIGS = 1.302 Å for the integration radius. Values in parenthesis for $V_{1\text{NN}}^{\text{Bader}}$ and $V_{2\text{NN}}^{\text{Bader}}$ provide the percentage difference relative to the bulk Fe atomic volume.

X_{Fe}	$\Delta q_X^{\text{Bader}}$ (e)	$\Delta q_{1\text{NN}}^{\text{Bader}}$ (e)	$\Delta q_{2\text{NN}}^{\text{Bader}}$ (e)	V_X^{Bader} (Å ³)	$V_{1\text{NN}}^{\text{Bader}}$ (Å ³)	$V_{2\text{NN}}^{\text{Bader}}$ (Å ³)	$\Delta q_{1\text{NN}}^{\text{DOS}}$ (e)	$\Delta q_{2\text{NN}}^{\text{DOS}}$ (e)
Ti	-1.004	0.100	0.089	9.642	11.645(2.76)	11.696(3.20)	0.026	-0.001
V	-0.576	0.061	0.083	10.649	11.464(1.16)	11.590(2.27)	0.023	0.011
Cr	-0.324	0.035	0.080	11.057	11.389(0.49)	11.567(2.07)	0.015	0.014
Mn	-0.154	0.037	0.061	11.377	11.419(0.76)	11.522(1.67)	0.010	0.010
Fe	0.000	0.000	0.000	11.333	11.333(0.00)	11.333(0.00)	0.000	0.000
Co	0.184	-0.022	0.056	11.670	11.314(-0.16)	11.549(1.91)	-0.015	0.001
Ni	0.360	-0.035	0.045	12.145	11.321(-0.10)	11.548(1.90)	-0.024	-0.003
Cu	0.281	-0.028	0.043	11.852	11.336(0.03)	11.556(1.97)	-0.018	-0.006
Zr	-1.077	0.103	0.056	12.749	11.619(2.53)	11.652(2.82)	0.038	-0.018
Nb	-0.708	0.063	0.050	13.480	11.411(0.70)	11.546(1.88)	-0.024	-0.003
Mo	-0.201	0.026	0.043	14.191	11.265(-0.60)	11.466(1.18)	0.040	0.003
Tc	0.191	-0.006	0.034	14.808	11.174(-1.40)	11.432(0.88)	0.031	0.004
Ru	0.516	-0.052	0.024	15.246	11.112(-1.95)	11.453(1.06)	0.008	-0.004
Rh	0.600	-0.055	0.010	15.241	11.194(-1.22)	11.470(1.22)	-0.013	-0.016
Pd	0.635	-0.073	-0.003	15.428	11.202(-1.15)	11.488(1.37)	-0.025	-0.027
Ag	0.474	-0.049	0.000	15.212	11.301(-0.28)	11.552(1.94)	-0.020	-0.034
Hf	-0.996	0.096	0.054	12.788	11.569(2.08)	11.621(2.55)	0.045	-0.014
Ta	-0.700	0.077	0.043	13.734	11.402(0.61)	11.496(1.45)	0.055	-0.003
W	-0.216	0.051	0.026	14.876	11.272(-0.53)	11.390(0.51)	0.058	0.004
Re	0.328	-0.018	0.020	16.048	11.069(-2.33)	11.373(0.35)	0.051	0.004
Os	0.730	-0.058	-0.001	16.887	11.003(-2.91)	11.340(0.07)	0.031	-0.002
Ir	0.973	-0.081	-0.019	17.391	11.027(-2.70)	11.350(0.15)	0.007	-0.015
Pt	1.010	-0.102	-0.030	17.588	11.039(-2.59)	11.374(0.36)	-0.012	-0.028
Au	0.920	-0.069	-0.035	17.708	11.200(-1.17)	11.419(0.76)	-0.016	-0.038

As noted in Sec. III A, atoms of group IV metals are systematically undersized when substituted into either Fe or W. It is apparent from Tables VIII and IX that the Bader charge difference of all group IV solutes is $\sim -1e$ in both Fe and W. We posit that one of the two $(n-1)d$ electrons on the solute is distributed to the surrounding host lattice, significantly reducing the degree to which the positive charge of the nucleus is screened by the valence d shell. Thus, there is a stronger attraction between the nucleus and the outer ns electrons, resulting in the observed undersizing of group IV solutes.

As shown in Tables VIII and IX, the change in Bader charges of the substitutional solute can be attributed to the charge transfer to its first- and second-NNs.

The Bader volumes of the first-NN tungsten atoms are smaller than those in bulk. For the $4d$ and $5d$ transition metals, where the magnetovolume effect is less pronounced, the Bader and Voronoi volumes show that if the first-NN tungsten atoms increase their volume, the second-NN atoms would decrease. Since their contributions cancel each other, the volumes are comparable to the estimated metallic radius.

On the other hand, for transition metals in an iron matrix, the first- and second-NN iron atoms with a smaller group number have an increase in occupation for the s , p , and d electrons. This indicates that the atoms have a relatively larger volume, as evidenced by both Voronoi and Bader volumes, which contribute positively to the relaxation volume. The

solute atom appears to be elastically larger, as shown in Fig. 6. Ti_{Fe} is an exception. The occupation of the p valence electrons in the second-NN and the d valence electrons in the first-NN are reduced. It is the only $3d$ series transition metal whose relaxation volume is not anomalously oversized in iron.

The first- and second-NN Fe atoms around Co_{Fe} and Ni_{Fe} substitutions also show reduced occupation, yet the overall complexes are oversized relative to the metallic radius. This suggests that a magnetovolume effect of the solute atom dominates the behavior of these two strongly ferromagnetic elements. Indeed, both the Voronoi and Bader volumes of these transition metals exceed their respective metallic volumes.

However, this pattern does not hold universally. The Bader and Voronoi volume analyses reveal that the overall relaxation volume can be governed by the collective effects of neighboring atoms rather than the solute alone. Considering Cr_{Fe} as an example, both the Bader and Voronoi metrics indicate that the volume occupied by the Cr atom itself is smaller than that of an Fe atom. The positive relaxation volume, indicating that the complex is 20% larger than expected, therefore arises from charge transfer and subsequent expansion of the neighboring iron atoms. Notably, the Bader and Voronoi volume calculations disagree on whether the volume increase occurs primarily in the first- and second-NN Fe atoms.

TABLE IX. Charge difference (Δq^{Bader}) and Bader volumes (V^{Bader}) of transition metals and their first- and second-nearest neighbors when substituted into bcc W according to the Bader analysis. Charge differences computed using the density of states (Δq^{DOS}) are provided for comparison. Differences in the Bader charge are relative to the number of valence electrons (see Table I). Differences in the DOS charges of tungsten atoms neighboring the solute are relative to its value in perfect bulk (5.541e) using an RWIGS = 1.455 Å for the integration radius. Values in parenthesis for V_{1NN}^{Bader} and V_{2NN}^{Bader} provide the percentage difference relative to the bulk W volume.

X_W	$\Delta q_X^{\text{Bader}}$ (e)	$\Delta q_{1NN}^{\text{Bader}}$ (e)	$\Delta q_{2NN}^{\text{Bader}}$ (e)	V_X^{Bader} (Å ³)	V_{1NN}^{Bader} (Å ³)	V_{2NN}^{Bader} (Å ³)	$\Delta q_{1NN}^{\text{DOS}}$ (e)	$\Delta q_{2NN}^{\text{DOS}}$ (e)
Ti	-1.031	0.033	0.104	9.963	16.259(1.95)	16.418(2.94)	-0.019	-0.007
V	-1.357	0.048	0.108	7.980	16.318(2.31)	16.351(2.52)	-0.023	0.009
Cr	-0.319	-0.059	0.102	11.497	15.905(-0.27)	16.299(2.19)	-0.029	0.016
Mn	-0.057	-0.069	0.090	12.152	15.923(-0.16)	16.313(2.28)	-0.032	0.004
Mn [†]	-0.047	-0.074	0.095	12.095	15.864(-0.53)	16.295(2.17)	-0.032	0.014
Fe	0.119	-0.084	0.086	12.364	15.899(-0.31)	16.308(2.25)	-0.040	0.005
Fe [†]	0.117	-0.072	0.074	12.335	15.893(-0.35)	16.255(1.92)	-0.034	0.008
Co	0.218	-0.082	0.083	12.430	15.908(-0.26)	16.331(2.40)	-0.042	0.001
Co [†]	0.212	-0.078	0.080	12.373	15.893(-0.35)	16.312(2.28)	-0.038	0.002
Ni	0.242	-0.074	0.078	12.274	15.943(-0.03)	16.343(2.47)	-0.045	-0.004
Cu	0.135	-0.019	0.073	12.017	16.146(1.24)	16.387(2.75)	-0.048	-0.016
Zr	-1.172	0.071	0.083	12.585	16.309(2.26)	16.398(2.82)	-0.010	-0.023
Nb	-0.735	0.047	0.068	13.598	16.171(1.40)	16.254(1.91)	-0.010	-0.009
Mo	-0.044	-0.055	0.052	15.085	15.829(-0.75)	16.141(1.21)	-0.015	0.004
Tc	0.339	-0.081	0.055	15.832	15.755(-1.22)	16.147(1.25)	-0.020	0.005
Ru	0.592	-0.050	0.045	16.255	15.861(-0.55)	16.168(1.38)	-0.022	-0.004
Rh	0.743	-0.059	0.033	16.405	15.851(-0.61)	16.193(1.53)	-0.026	-0.017
Pd	0.717	-0.057	0.025	16.154	15.911(-0.24)	16.223(1.72)	-0.037	-0.028
Ag	0.479	-0.047	0.033	15.574	15.996(0.30)	16.314(2.29)	-0.043	-0.040
Hf	-1.099	0.072	0.082	12.661	16.294(2.16)	16.389(2.76)	-0.002	-0.024
Ta	-0.693	0.056	0.053	14.078	16.152(1.28)	16.187(1.50)	0.003	-0.010
W	0.000	0.000	0.000	15.949	15.949(0.00)	15.949(0.00)	15.949	0.000
Re	0.572	-0.088	0.022	17.426	15.673(-1.73)	16.020(0.45)	-0.007	0.003
Os	0.977	-0.084	0.024	18.393	15.690(-1.62)	16.065(0.73)	-0.011	-0.003
Ir	1.153	-0.085	0.003	18.768	15.697(-1.58)	16.065(0.73)	-0.013	-0.018
Pt	1.130	-0.081	-0.002	18.568	15.754(-1.22)	16.112(1.03)	-0.022	-0.033
Au	0.938	-0.071	0.001	18.117	15.850(-0.62)	16.180(1.45)	-0.034	-0.044

The relaxation volumes of solutes in W and Fe are plotted against their Bader charge differences in Figs. 15 and 16, revealing a nonlinear correlation between the change in electronic structure of the solute atom and the resulting dilatation of the host bcc crystal. For both W and Fe, relaxation volumes of 3d elements are weakly correlated with the change in solute charge, whereas the 4d and 5d solutes exhibit a hook shaped trend: Ω_{rel} falls and $\Delta q_X^{\text{Bader}}$ rises with increasing group number until it reaches a minimum at group VIII, after which $\Delta q_X^{\text{Bader}}$ decrease and relaxation volumes become more positive from groups IX to XI.

E. Enthalpy of mixing

Using *ab initio* calculations, we can compute the enthalpy of mixing for the various solute atoms in Fe and W lattices. The enthalpy of mixing represents the relative change in energy when one substance dissolves in another at a given concentration. At zero external pressure, as in our DFT calculations, the enthalpy of mixing ΔH_{mix} is equal to the energy of mixing. For a binary system containing N_B atoms of species B and N_A atoms of species A, the enthalpy of mixing per atom

is therefore

$$\Delta H_{\text{mix}} = \frac{E[N_A A + N_B B] - N_A E[A] - N_B E[B]}{N_A + N_B}, \quad (23)$$

where $E[N_A A + N_B B]$ is the total energy of the mixed system, and $E[A] = E[N_A A]/N_A$ and $E[B] = E[N_B B]/N_B$ are energies per atom of the reference compounds, composed of elements A or B, respectively.

In Eq. (23), the negative value of the mixing enthalpy implies an exothermic mixing process, indicating that energy is released during mixing. Conversely, a positive mixing enthalpy corresponds to an endothermic reaction that fundamentally favors elemental segregation [151]. More negative mixing enthalpy indicates stronger affinity of the two elements toward formation of an alloy.

In this work, we only consider the highly dilute alloy, where $N_A \gg N_B$ and $N_B = 1$ in all the supercell calculations. In this impurity limit, the values given by Eq. (23) become very small, and a better defined quantity, not vanishing in the $N_A \gg 1$ limit, is [152]

$$E_{\text{sol}} = (N_A + 1)\Delta H_{\text{mix}} = E[N_A A + B] - N_A E[A] - E[B]. \quad (24)$$

TABLE X. Volumes determined using the Voronoi tessellation for solute transition metals in bcc Fe (V_X^{Voronoi}) as well as for Fe atoms in the first- and second-nearest neighbor positions to the substituted atom. Values in parentheses provide the percentage change from the Voronoi volume of an Fe atom in the perfect lattice.

X_{Fe}	V_X^{Voronoi} ($\text{\AA}^3$)	V_{1NN}^{Voronoi} ($\text{\AA}^3$)	V_{2NN}^{Voronoi} ($\text{\AA}^3$)
Ti	11.772	11.434(0.89)	11.436(0.92)
V	11.405	11.367(0.30)	11.345(0.11)
Cr	11.314	11.341(0.07)	11.318(-0.13)
Fe	11.333	11.333 (0.00)	11.333 (0.00)
Mn	11.399	11.327(-0.05)	11.329(-0.03)
Co	11.322	11.355(0.20)	11.336(0.03)
Ni	11.479	11.372(0.35)	11.367(0.30)
Cu	11.552	11.366(0.30)	11.381(0.42)
Zr	12.542	11.629(2.62)	11.633(2.65)
Nb	12.143	11.546(1.89)	11.531(1.75)
Mo	11.781	11.461(1.13)	11.438(0.93)
Tc	11.660	11.422(0.79)	11.405(0.64)
Ru	11.742	11.445(1.00)	11.432(0.88)
Rh	11.913	11.492(1.41)	11.481(1.31)
Pd	12.177	11.538(1.81)	11.545(1.87)
Ag	12.423	11.566(2.06)	11.605(2.41)
Hf	12.435	11.588(2.26)	11.609(2.44)
Ta	12.072	11.518(1.64)	11.515(1.61)
W	11.794	11.459(1.11)	11.445(0.99)
Re	11.694	11.431(0.87)	11.418(0.75)
Os	11.759	11.442(0.97)	11.436(0.91)
Ir	11.942	11.496(1.45)	11.492(1.40)
Pt	12.195	11.553(1.95)	11.557(1.98)
Au	12.517	11.602(2.37)	11.635(2.67)

In what follows, we refer to this quantity as the solution energy E_{sol} .

To benchmark the enthalpy of mixing for constrained functional DFT calculations, we compare it with the well-

TABLE XI. Volumes determined using the Voronoi tessellation for solute transition metals in bcc W (V_X^{Voronoi}) as well as for W atoms in first- and second-nearest neighbor positions to the substituted atom. Daggered rows provide data for the nonmagnetic metastable states. Values in parentheses provide the percentage change from the Voronoi volume of a W atom in the perfect lattice.

X_{W}	V_X^{Voronoi} ($\text{\AA}^3$)	V_{1NN}^{Voronoi} ($\text{\AA}^3$)	V_{2NN}^{Voronoi} ($\text{\AA}^3$)
Ti	15.986	15.925(-0.15)	15.962(0.08)
V	15.648	15.857(-0.57)	15.879(-0.44)
Cr	15.526	15.818(-0.82)	15.848(-0.63)
Mn	15.689	15.830(-0.75)	15.890(-0.37)
Mn [†]	15.572	15.793(-0.98)	15.857(-0.58)
Fe	15.665	15.827(-0.76)	15.888(-0.38)
Fe [†]	15.641	15.782(-1.04)	15.875(-0.46)
Co	15.728	15.808(-0.88)	15.902(-0.29)
Co [†]	15.690	15.784(-1.03)	15.892(-0.36)
Ni	15.753	15.802(-0.92)	15.914(-0.22)
Cu	15.937	15.840(-0.68)	15.963(0.09)
Zr	16.590	16.094(0.91)	16.109(1.00)
Nb	16.218	16.016(0.42)	16.016(0.42)
Mo	15.926	15.941(-0.05)	15.944(-0.03)
Tc	15.884	15.897(-0.32)	15.928(-0.13)
Ru	16.019	15.867(-0.51)	15.959(0.06)
Rh	16.151	15.865(-0.52)	15.998(0.31)
Pd	16.269	15.904(-0.28)	16.038(0.56)
Ag	16.477	15.967(0.11)	16.095(0.92)
Hf	16.523	16.066(0.74)	16.096(0.92)
Ta	16.189	16.004(0.35)	16.011(0.39)
W	15.949	15.949(0.00)	15.949(0.00)
Re	15.907	15.927(-0.13)	15.940(-0.05)
Os	16.015	15.888(-0.38)	15.956(0.05)
Ir	16.207	15.877(-0.45)	16.009(0.38)
Pt	16.365	15.909(-0.25)	16.058(0.69)
Au	16.551	15.981(0.20)	16.112(1.03)

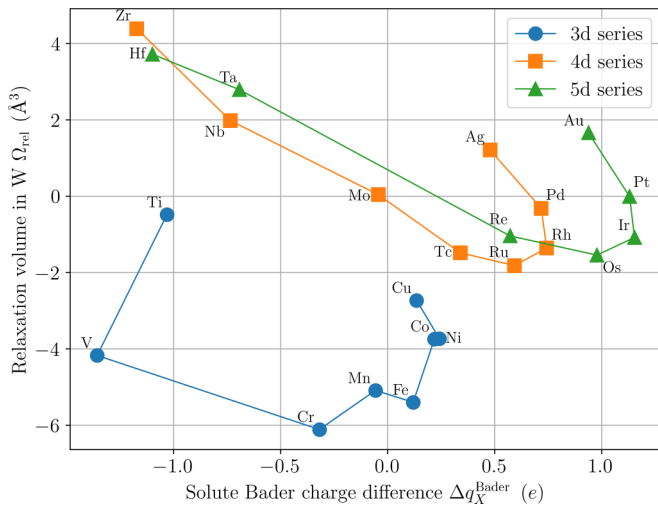


FIG. 15. Plot of solute relaxation volume against the solute Bader charge difference in W. Data points are connected according to the period of the solute, tracing out hook-shaped paths along which the elements are sorted by group number.

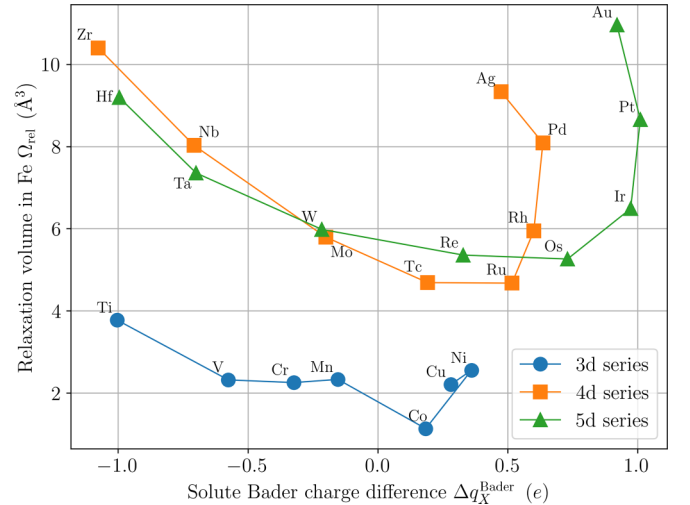


FIG. 16. Plot of solute relaxation volume against the solute Bader charge difference in Fe. Data points are connected according to the period of the solute, tracing out hook-shaped paths along which the elements are sorted by group number.

TABLE XII. Solution energy E_{sol} for transition metal impurities in bcc W and bcc Fe calculated using 250-atom simulation cells with a single on-site substitution (in eV per solute atom units). Values given in parenthesis for Mn_W , Fe_W , and Co_W are the mixing enthalpies for the meta-stable nonmagnetic states of the impurity atom. The impurity concentration is 0.4% in these zero pressure calculations, representing the mixing energy per solute atom in the dilute limit, cf. Eqs. (23) and (24). For transition metals where the lowest energy crystal structure is bcc, bold symbols are used.

Lattice	Period	Group							
		4	5	6	7	8	9	10	11
W	3d	−0.86	−0.43	0.40	0.46 (0.64)	0.79 (1.28)	0.98 (1.15)	0.99	1.37
	4d	0.07	−0.24	0.48	0.02	0.19	0.54	1.24	2.40
	5d	−0.36	−0.45	0.00	−0.16	−0.16	0.10	0.79	1.97
Fe	3d	−0.87	−0.71	−0.13	0.08	0.00	−0.23	0.01	0.69
	4d	0.23	−0.06	0.06	−0.13	−0.30	−0.34	0.39	1.81
	5d	−0.23	−0.07	−0.01	−0.36	−0.65	−0.83	−0.36	0.95

documented energy of solution computed for Cr substitution in Fe. The dissolution of Cr in Fe is exothermic for $x \leq 10\%$, and this is reflected in the negative heat of solution [109,153] associated with magnetic frustration [6,109,154]. The reference energies for bcc Fe and Cr lattices correspond to their ferromagnetic and antiferromagnetic magnetically ordered states, respectively.

The solution energy evaluated using a magnetically noncollinear 54-atom configuration is $E_{\text{sol}} = -0.16$ eV (equivalent to $\Delta H_{\text{mix}} = -3$ meV/atom for $N_A + N_B = 54$). For a 250-atom collinear configuration, the solution energy is -0.12 eV. This agrees with other literature data, reporting solution energies from -0.12 eV for published PAW calculations to -0.47 eV for cases using harder pseudopotentials [155]. Repeating the calculation using the collinear formalism and a 54-atom cell also yields $E_{\text{sol}} = -0.16$ eV, matching literature results for the same simulation cell size [153]. This confirms the consistency between spin-polarized DFT and spinor representations of noncollinear DFT calculations. The relative error for mixing energy in small-cell noncollinear calculations corresponds to higher solute concentration yet remains accurate for calculating the mixing enthalpy even at 1.85% concentration. For tungsten, we compare the enthalpy of mixing for V and Ta substitutional impurities to the data from Ref. [156]. For small simulation cells, where the V_W concentration is 1.85%, the DFT calculations performed by Muzyk *et al.* [156] predicted the mixing enthalpy of ~ -10 meV/atom, and this value agrees with our results.

Energies of solution for various substitutional atoms, calculated using 250-atom simulation cells for both W and Fe host lattices, are summarized in Table XII and Fig. 17. Except for Mo_W , our results show good quantitative agreement with results of DFT calculations reported in literature [29]. Small differences likely arise from different GGA exchange-correlation functionals, known to be responsible for some quantitative differences in the predicted properties of tungsten, such as lattice parameters and SIA formation energies.

For the enthalpy of mixing calculations, reference configurations are nonmagnetic bcc structures, except for Mn, Fe, Co, and Ni, which are ferromagnetic, and Cr, which is taken to be antiferromagnetic.

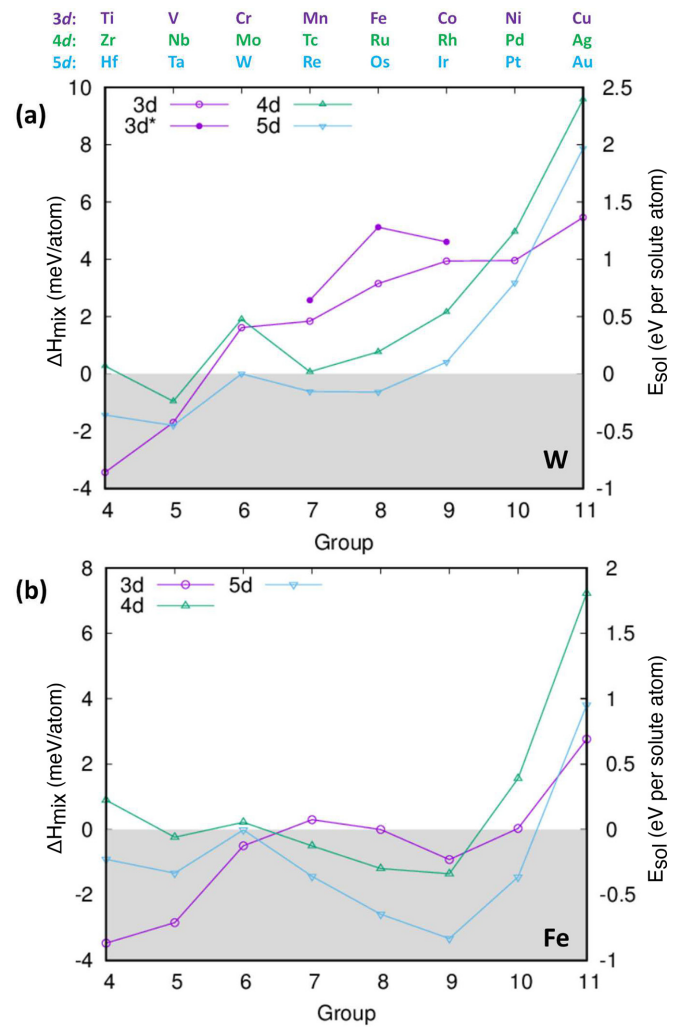


FIG. 17. Enthalpy of mixing (left y axis) and solution energy (right y axis) for 3d, 4d, and 5d transition metal series substitutions in bcc W (a) and bcc Fe (b). The values were calculated using a 250-atom cell ($5 \times 5 \times 5$ unit cells). For the 3d series substitutions Mn_W , Fe_W , and Co_W , we additionally show the energy of solution for the metastable nonmagnetic states of the solute atoms (labelled 3d*, solid circles).

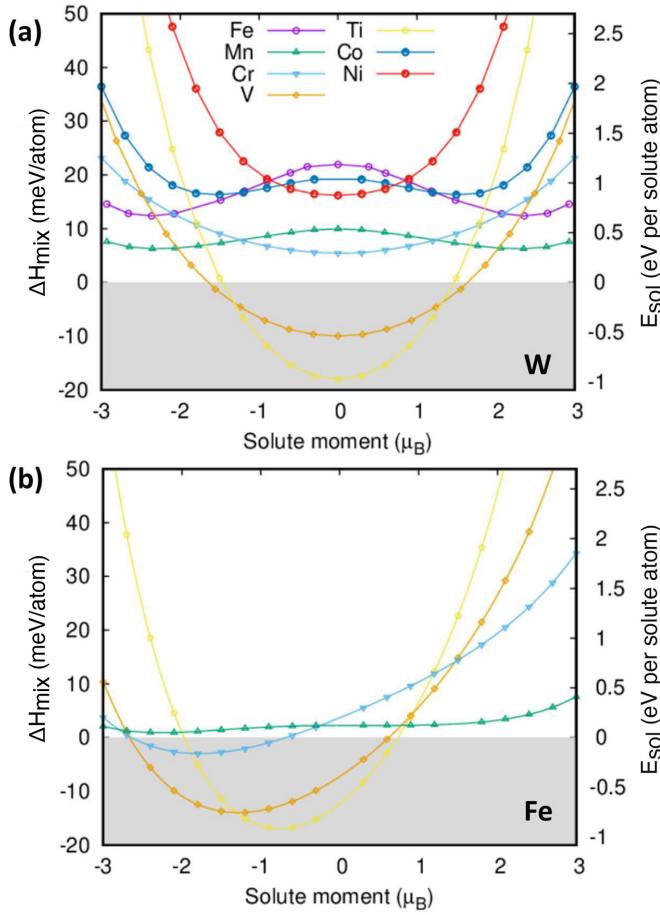


FIG. 18. Enthalpy of mixing (left y axis) and solution energy (right y axis) for dilute 3d series transition metal substitutions in W and Fe bcc lattices as a function of changes in the magnetic moment of solute enforced using a constrained density functional. The corresponding solute concentration is 1.85%.

For both W and Fe, the energies of solution exhibit an approximate asymmetric double-well form with respect to increasing group number of transition metal substitutions. A local maximum occurs for group 6 substitutions in 5d and 6d series transition metals in both host lattices. A pronounced minimum in E_{sol} exists for group 9 solute substitution in Fe. The alloying ability sharply reduces for groups 10 and 11 in both host materials.

Re_W and Os_W are the only the midblock transition metals with negative solution energies in W. In addition, they are common transmutation products forming in tungsten under neutron irradiation. These elements have been recently shown to decorate voids in neutron-irradiated samples [157–160]. Ta_W , despite the fact that it also exhibits a negative energy of solution [29,156], does not appear to decorate voids [161]. This may be attributed to its stronger affinity to alloying and its interactions with vacancies, which are not considered here but are treated in detail in Ref. [161].

In Fig. 18, we analyze the enthalpy of mixing as a function of the magnetic moment of the solute transition metal. Minima in ΔH_{mix} necessarily correspond to magnetic moments that minimize the total energy. For W, all solutes that retain magnetic moments (i.e., Mn, Fe, and Co) are insoluble at

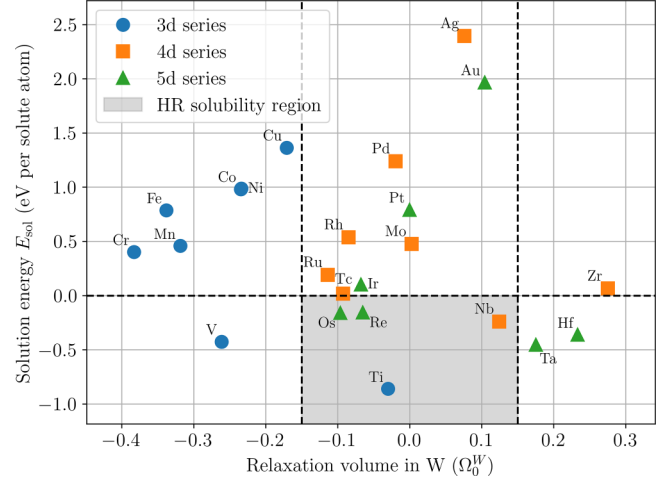


FIG. 19. Two-dimensional map of solution energies and relaxation volumes of transition metal atoms substituted in W. Element data points are colored and assigned markers according to their period in the periodic table. The Hume-Rothery solubility region $|\Omega^{\text{rel}}| \lesssim 0.15$ is shaded in grey.

0 K and exhibit local maxima for the enthalpy of mixing in nonmagnetic states. The difference in enthalpies of mixing between magnetic and nonmagnetic states is significantly larger for smaller simulation cells with higher solute concentrations, indicating a strong influence of magnetic interactions on solubility.

Figure 18 also shows a strong dependence of the enthalpies of mixing on the solute magnetic moment, similar to the magnetovolume effect shown in Sec. III B. Magnetic configurations of Mn_W , Fe_W , and Co_W have larger relaxation volumes and smaller enthalpies of mixing than metastable nonmagnetic states that minimize relaxation volume.

For example, in the magnetic ground state of the Fe_W system, where $E_{\text{sol}} = 0.79$ eV, the solute atom volume $\Omega_W^{\text{Fe}} = 10.554 \text{ \AA}^3$ is larger than the $8.941 \text{ \AA}^3$ volume of Fe in the metastable non-magnetic state whose solution energy is 1.28 eV. Ω_W^{Fe} is defined and tabulated in Eq. (5) and Table IV, respectively.

These results indicate that solubility may diminish in the presence of high magnetic fields that alter the magnetic moment of the solute atom. However, caution is needed since we have not addressed how the applied magnetic field would affect beyond the targeted substitution. For example, in higher concentration alloys, screening from the alloy background will become a non-negligible factor. Besides, the free energy contributions at finite temperature will alter the mixing enthalpy.

Figures 19 and 20 show little to no correlation between the solubility of a transition metal and the relaxation volume it produces in bcc W or Fe. Furthermore, the range of soluble relaxation volumes $|\Omega^{\text{rel}}| \lesssim 0.15$ according to the Hume-Rothery rules, shaded in grey, appear to be a poor indicator of solubility for both host metals.

The relative increase in the energy of solution for transition metals in the middle of the d block can be attributed to the sharing of the same bcc ground state. In contrast, transition metals with fcc or hcp structures require additional energy

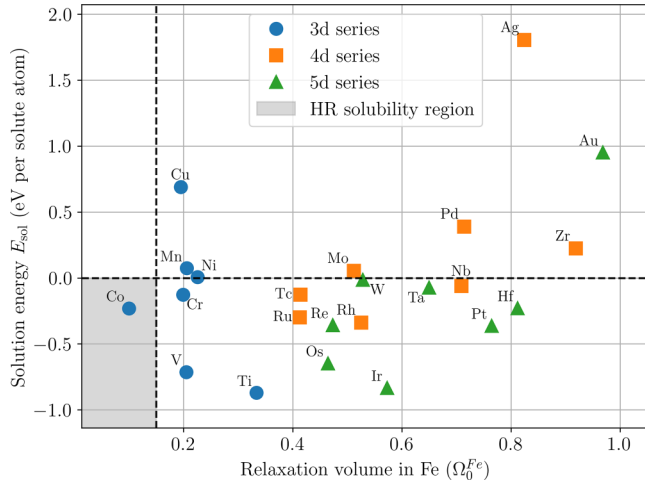


FIG. 20. Two-dimensional map of solution energies and relaxation volumes of transition metal atoms substituted in Fe. Element data points are colored and assigned markers according to their period in the periodic table. The Hume-Rothery solubility region $|\Omega^{\text{rel}}| \lesssim 0.15$ is shaded in grey.

for adapting a structural phase change. The same argument holds for Mn_{Fe} whose ground state is a noncollinear A12 configuration [128].

IV. CONCLUSION

Relaxation volumes were systematically calculated for substitutional solute of 3d, 4d, and 5d series transition metals in bcc Fe and bcc W lattices. We performed substantive analyses considering the metallic volume, Bader volume, and Voronoi volume of the solute atom and its first-, second-, and third-nearest-neighbor host atoms. Chemical effects at the first- and second-nearest neighbors were shown to additionally contribute to the relaxation volume of substitutional solute.

In bcc iron, the solute impurities were found to act elastically and significantly oversized relative to their volume in bulk. A striking example is Au_{Fe} , which appears 33% larger by volume in Fe relative to its metallic volume. Cr_{Fe} , which in its bulk crystalline form only has a 0.3% lattice mismatch to Fe, is found to relax to be 20% larger in volume than the host Fe atoms upon substitution. This anomalous elastic oversizing suggests why even small concentrations of Cr can increase the retention of defects in irradiated FeCr alloys.

In bcc tungsten, 3d series transition metal substitutions are undersized, while the 4d and 5d series substitutions remain comparable to their metallic volumes. The enthalpy of mixing was investigated as a function of the magnetic moment of the substitution. The volume of Fe_{W} is 11% smaller in the W lattice with an energy of solution of 0.77 meV/atom, accounting for its tendency to be attracted to elastically compressed regions such as grain boundaries and dislocation loops and out of the bulk. The relaxation volume is found to decrease further if the Fe_{W} solutes magnetic moment is quenched.

A constrained density functional theory method for non-collinear magnetism is used to show a magnetovolume effect contributes to the anomalous size of the solute metals. The relaxation volumes of solute atoms in W are minimized when their magnetic moments are suppressed by the constraint field. Local density of states from electronic structure calculations shows how W atoms near 3d series solutes effectively shrink due to a small reduction in the occupancy of its local electron density. On the other hand, Fe atoms neighboring the impurity atom swell. These neighbor effects also contribute to the observed anomalous elastic size.

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Views and opinions expressed are, however, those of the authors only and do not necessarily reflect those of the European Union or the European Commission. Neither the European Union nor the European Commission can be held responsible for them.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. To obtain further information on the data and models underlying the paper please contact Publications-Manager@ukaea.uk.

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