

Vacancy formation and migration energies in 15-15Ti and FeCrAl: A study from first principles

Nils Wikström^{1,*}, Ruihuan Li,² Stephan Schönecker,² Xiaoqing Li,² and Pär Olsson^{1,†}

¹Department of Physics, Nuclear Science and Engineering, *KTH Royal Institute of Technology*, Stockholm, Sweden

²Department of Materials Science and Engineering, *KTH Royal Institute of Technology*, Stockholm, Sweden

 (Received 17 July 2026; revised 13 September 2026; accepted 28 September 2026; published 23 October 2026)

Lead-cooled fast reactors impose harsh environments on the structural materials, including high damage doses, high temperatures and corrosive liquid lead. To withstand these environments, advanced steel concepts, such as a composite of 15-15Ti and FeCrAl, have been proposed as fuel cladding. Microstructural evolution of alloys is governed by fundamental properties, including the vacancy formation and migration energies, yet such data for novel alloy compositions is sparse. In this work, an extensive set of vacancy formation and migration energies in two alloys, 15-15Ti and FeCrAl, was calculated from first principles, employing density functional theory. Special quasirandom structures were generated for both alloys, and different magnetic states of the alloys were simulated. It was found that the vacancy formation energy is highly influenced by the chemical and magnetic environment in 15-15Ti, while in FeCrAl the size mismatch between Fe and the alloying elements dominates. The vacancy formation energy was calculated by two different density functional theory formulations, showing excellent agreement. The vacancy migration energy was found to be governed by changes in the magnetic and chemical environment as the atom migrates. Based on these findings, temperature-averaged behaviors of vacancies in the alloys are derived, which can be further used to define effective vacancy formation and migration energies at reactor-relevant temperatures. The effective vacancy formation and migration energies can be used to predict temperature-variable shifts needed to accommodate the higher dose rate when using ion irradiation to emulate neutron irradiation.

DOI: [10.1103/tz5y-dzyb](https://doi.org/10.1103/tz5y-dzyb)

I. INTRODUCTION

To improve safety, sustainability, and fuel-cycle efficiency of nuclear energy systems, the Generation IV International Forum was founded. Among the Generation IV concepts, lead-cooled fast reactors (LFRs) are considered favorable due to their neutronic performance, inherent safety characteristics, and compatibility with closed fuel cycles [1]. LFRs impose harsh environments for structural materials, which face high damage doses and corrosive environments [2], leading to numerous suggestions for different structural materials employed in fast reactors [3]. Candidate cladding and structural alloys include a variety of steels, such as ferritic alumina-forming steels, known for their excellent corrosion resistance [4], and Ni-stabilized austenitic steels, which are long-studied core materials in fast-reactor systems [5]. Specifically, an LFR being developed within the SUNRISE Centre [6,7] will feature overlay-welded FeCrAl on a 15-15Ti cladding tube, due to the high radiation dose

limit and desirable mechanical properties of 15-15Ti [8] combined with the excellent corrosion resistance of FeCrAl in liquid lead [9]. In the reactor environment, the cladding will have to withstand high temperatures up to 600 °C, large temperature gradients, neutron irradiation, mechanical stress, interactions with fission products, and erosion-corrosion from the liquid lead [10], accelerating the microstructural evolution [11]. The combination of these effects can cause creep, swelling, and irradiation-induced segregation, degrading the materials over time. Many of the aforementioned effects are well understood on the macroscopic scale in the materials, but the mechanisms of clustering and microstructural evolution are governed by fundamental properties, such as vacancy formation energies and vacancy migration energies. Studying such effects with experimental procedures can be costly, both from an economic perspective and in terms of time investment [12,13]. To accelerate the qualification process, atomistic modeling will play an important role in the prediction of microstructural evolution, providing mechanistic understanding and helping to better focus experimental efforts [14].

To this end, density functional theory (DFT) [15,16] simulations can be used to predict the agglomeration and diffusion of vacancies by calculating the vacancy formation and migration energies, enabling a thorough theoretical understanding of clustering mechanisms. However, calculating such quantities in ternary alloys poses a significant technical challenge due to disordering complexity, the influence of local environments, and complex magnetic structures. The vacancy

*Contact author: nilwik@kth.se

†Contact author: polsson@kth.se

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI. Funded by [Bibsam](https://www.bibsam.se/).

formation and migration energies are not limited to a single value, but rather a statistical distribution. The effect of local environment can be evaluated by sampling a sufficiently large number of sites in the supercells and analyzing how the first or second nearest neighbors influence the formation and migration energies [17]. Moreover, distributions are often noisy due to many competing effects, and accurate descriptors must be developed and employed.

An additional complication arises from the magnetic structure of Fe-based alloys. The ground state of pure Fe is ferromagnetic (FM), whereas Cr exhibits a complicated structure, often represented by an antiferromagnetic (AFM) ordering in DFT [15,16]. In Fe-based alloys, Cr tends to couple antiferromagnetically with neighboring Fe atoms [18]. Adding Al to this system is generally not troubling, as Al shows weak magnetic coupling and small local moments [19] that generally reduce the average magnetic moment, which stabilizes the ferritic phase. In contrast, adding enough Ni to an FeCr alloy changes the crystal structure to face-centered cubic (fcc) and the magnetic structure from FM to paramagnetic (PM) at relevant operating temperatures, relaxing the magnetic moments of the Fe atoms. This has been successfully modeled using disordered localized moments (DLM) with the coherent potential approximation (CPA) in DFT simulations [20]. The different magnetic behaviors of Cr and Ni in FeCrNi alloys create a large number of magnetic states, all close in energy, which makes convergence toward a single magnetic state challenging [21]. Therefore, it is often practical to perform DFT calculations of point defect energies in the low-temperature ground state of the FeCrNi alloy [17], this being the single-layer AFM state.

In binary alloys, several studies of vacancy formation and migration energies exist [22,23], and local environment can readily be analyzed by substituting one, or several, of the neighbors with the alloying element. This has been successfully used to model dilute alloy systems [22,24]. In concentrated ternary alloys, however, the available data is sparse [17,25,26] and limited mainly to specific compositions of austenitic, Ni-stabilized steels, with limited analysis of local environmental effects. To our knowledge, no data exists on migration or formation energies of vacancies in concentrated ferritic FeCrAl steels or austenitic Fe-15Cr-15Ni steels. Furthermore, the macroscopic thermodynamic behavior of vacancy formation and migration is not described by linear functions, but rather exponential functions in the form of rates or probabilities. Therefore, an effective activation energy must be defined from the ensemble-averaged Boltzmann factor rather than from the arithmetic average [27]. Taking the arithmetic average of such quantities will yield unphysically large effective barriers with significant consequences on kinetic behavior. For instance, a 0.5 eV barrier leads to jump frequencies that are roughly three orders of magnitude higher than for 1.0 eV barriers at relevant reactor operating temperatures [28,29].

In order to fill these gaps, we evaluate the vacancy formation and migration energies in two different alloys: 15-15Ti and FeCrAl. Electronic structure calculations using DFT [15,16,30] are utilized to predict the energies. Supercells of fcc and body-centered cubic (bcc) lattices, consisting of 256 and 250 atoms, respectively, are created using

special quasirandom structures (SQS) [31] formed by the major alloying elements of 15-15Ti and FeCrAl. The alloy compositions studied are 70 at.% Fe, 15 at.% Cr, and 15 at.% Ni for 15-15Ti and 82 at.% Fe, 10 at.% Cr, and 8 at.% Al for FeCrAl, modeling the Kanthal EF100 alloy [9,24]. The trace, reactive, and interstitial elements incorporated in the real alloys are excluded from explicit consideration in these model systems. These ternary systems are nevertheless expected to capture the fundamental behavior of magnetic moments, formation and migration energies exhibited by the alloys. The vacancy formation energies are calculated by two different DFT methods: the plane-wave Vienna *ab initio* simulation package (VASP) [16,32–34], and the exact muffin-tin orbitals CPA (EMTO-CPA) [35,36], enabling comparison between the two. Additionally, the size mismatch between the alloying elements is calculated, and used as a basis to create a first-order model to predict vacancy formation energies. The vacancy migration energies are exclusively calculated from VASP. For each calculated quantity, correlations based on local chemical and magnetic environments are analyzed. Finally, the evaluated vacancy formation and migration energies are used to calculate an effective temperature-dependent activation energy for both these processes, and an effective temperature-dependent activation energy for diffusion, E_a , is derived. We then quantify the effect of thermodynamic averaging at different temperatures.

II. METHODOLOGY

A. Computational details

In this work, two sets of calculations were performed to find the vacancy formation and migration energies, using first-principles calculations, in two alloy models: 15-15Ti and FeCrAl. The vacancy formation energies were obtained using both the DFT code VASP, and the EMTO-CPA method, while the vacancy migration energies were calculated from VASP alone. Plotting and data-processing scripts were developed with the assistance of Claude Code (Anthropic).

VASP is a plane-wave code that utilizes the projector augmented wave (PAW) method [15]. The standard PAW potentials with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) were used [37]. To minimize the energy, the blocked-Davidson algorithm [38,39] was employed for the first few electronic steps, followed by RMM-DIIS [34] for the remaining electronic steps. A force-based convergence criterion was employed, stopping the ionic relaxation when the force on any atom was below 0.01 eV/Å. To sample the first Brillouin zone, a $2 \times 2 \times 2$ Monkhorst-Pack grid was utilized. First-order Methfessel-Paxton smearing was applied with smearing widths of 0.3 eV and 0.2 eV, for 15-15Ti and FeCrAl, respectively. The plane-wave energy cutoffs were adapted to each calculation, ensuring accurate convergence on the order of 1 meV/atom and enabling comparison with previous studies [17,40]. The convergence tests resulted in choosing energy cutoffs of 300 eV for 15-15Ti and 400 eV for FeCrAl in the vacancy formation energy calculations, and 300 eV for 15-15Ti and 450 eV for FeCrAl in the vacancy migration energy calculations. All calculations were spin polarized.

For the VASP calculations, two supercells were designed as SQS [41] of the major alloying elements present in the two alloys. The austenitic supercell, for 15-15Ti, was constructed from $4 \times 4 \times 4$ replicas of a fcc unit cell, containing 180 Fe atoms (70 at.%), 38 Cr atoms (15 at.%), and 38 Ni atoms (15 at.%). The ferritic supercell, for FeCrAl, was constructed from $5 \times 5 \times 5$ replicas of a bcc unit cell, containing 205 Fe atoms (82 at.%), 25 Cr atoms (10 at.%), and 20 Al atoms (8 at.%). The lattice parameters for 15-15Ti and FeCrAl were initialized to 3.61 Å and 2.86 Å, respectively.

15-15Ti, which has a complicated magnetic structure, was initialized in an AFM state, alternating the magnetic moments in the (100) planes parallel and antiparallel. The initial magnetic moments were set to $\pm 3 \mu_B$ for Fe, and $\pm 1 \mu_B$ for Cr and Ni. The PM state of the austenitic 15-15Ti is very challenging to describe directly in a plane-wave supercell-based DFT framework due to its disordered nature. Therefore, we employed an AFM state to approximate a limit of the PM state, which preserves local magnetic moments while maintaining close to zero net magnetization. This approach has been widely used [17,20,21], as it provides a more realistic representation of the alloy than a nonmagnetic state. Moreover, as previously stated, ferritic Fe-Cr based alloys generally show AFM ordering with respect to the Fe and Cr atoms, while Al remains nonmagnetic. Therefore, FeCrAl was initialized in an AFM state, where the initial moments were set to $+3 \mu_B$ for Fe, $-1 \mu_B$ for Cr and $0 \mu_B$ for Al. Visualization of the magnetic moments, atomic structures and calculations of the Voronoi volumes was performed with the open visualization tool (OVITO) [42].

To efficiently sample a wide chemical range for predictions of the vacancy formation energies, EMTO-CPA calculations were employed. The compositions were $\text{Fe}_{1-x-y}\text{Cr}_x\text{Ni}_y$, where $x, y \leq 0.20$ and $\text{Fe}_{1-x-y}\text{Cr}_x\text{Al}_y$, where $x, y \leq 0.15$. For each alloy, x and y were increased independently in increments of 5 at.%, resulting in 25 different FeCrNi compositions and 16 different FeCrAl compositions. For the FeCrNi alloys, $2 \times 2 \times 2$ replicas of the conventional cell (32 atoms in the supercell) were employed together with a $13 \times 13 \times 13$ k-point mesh. For the FeCrAl alloys, bulk supercells containing 27 atoms were constructed as $3 \times 3 \times 3$ replicas of the bcc primitive cell and sampled using a $15 \times 15 \times 15$ k-point mesh. These settings ensured a stability of the vacancy formation energy, E_f^v , within ± 0.02 eV upon using denser k-point meshes or doubling the supercell size.

The EMTO method is an improved screened Korringa-Kohn-Rostoker method that solves the Kohn-Sham equations for optimized overlapping muffin-tin potentials by using a Green's function formalism [43]. The exchange-correlation effects were described using the PBE functional [37]. The scalar-relativistic approximation together with the soft-core scheme was employed, and the total energies were evaluated using the full charge-density technique. The muffin-tin basis set included s , p , d , and f orbitals, and the Green's functions were calculated for 16 complex energy points for the valence states below the Fermi level.

Chemical disorder was treated within the CPA [35,36], which describes substitutionally disordered alloys through an effective medium representing the configurational average of the alloy system. In this approach, the random alloy is re-

placed by a self-consistently determined effective medium possessing the symmetry of the underlying lattice. Consequently, local lattice relaxations, concentration fluctuations, and chemical short-range order effects are not considered. The calculated total energies and derived vacancy formation energies therefore correspond to configuration-averaged values.

The magnetic orderings used for $\text{Fe}_{1-x-y}\text{Cr}_x\text{Al}_y$ and $\text{Fe}_{1-x-y}\text{Cr}_x\text{Ni}_y$ in the EMTO calculations were chosen to be consistent with those employed for FeCrAl and 15-15Ti, respectively, in the VASP calculations. Additional calculations for $\text{Fe}_{1-x-y}\text{Cr}_x\text{Ni}_y$ were carried out assuming the paramagnetic state, which was described using the DLM model [44] and solved within the CPA. The DLM approach provides a first-principles mean-field description of spin-polarized electronic structures in the presence of randomly oriented local magnetic moments and has proven highly successful [45–47].

B. Vacancy formation energy

The first set of calculations, aimed to find the vacancy formation energy, was performed both with VASP and EMTO-CPA, to allow for comparison between the two methods and to validate the random sampling method utilized in this work. The VASP calculations were performed by fully relaxing the generated SQS, allowing relaxation of atomic positions, cell shape, and volume. Subsequently, a random atom was removed from the cell. With a vacancy introduced to the lattice, the cell was relaxed again, but exclusively allowing the atomic positions to update, resulting in the energy of the SQS with a defect. The vacancy formation energy was calculated by computing the difference between the energy of the defect lattice, E_{N-1} , and the perfect lattice, E_N . As these cells do not contain an equal number of atoms, the difference in energy must be compensated by the chemical potential of the removed element. The vacancy formation energy is then calculated as

$$E_f^v = E_{N-1} - (E_N - \mu_x), \quad (1)$$

where E_f^v is the vacancy formation energy, μ_x is the chemical potential with $x = \text{Fe, Cr, Al, or Ni}$, depending on which element was removed. To enable analysis of local environment, the process was repeated 96 times for 15-15Ti and 92 times for FeCrAl. If E_{N-1} is taken as the energy of the first self-consistent step during the second relaxation, the unrelaxed vacancy formation energy is found.

The chemical potential was calculated by fully relaxing systems of Fe, Cr, Al, and Ni, containing two or four atoms depending on the crystal structure. These calculations employed more dense k-point sampling, using a $14 \times 14 \times 14$ Monkhorst-Pack grid, and converging the force on any atom to below 0.001 eV/Å, yielding an accurate energy-per-atom reference for each atom.

Similarly, unrelaxed vacancy formation energies within the EMTO-CPA calculations were determined from the total energy difference between a supercell containing a monovacancy, E_{N-1} , and a bulk reference supercell with N atomic sites at equilibrium, E_N , corrected for the difference in the number of sites between the two supercells:

$$E_f^v = E_{N-1} - \frac{N-1}{N} E_N. \quad (2)$$

The bulk equilibrium volumes of the alloys were obtained by fitting a Morse-type function to seven calculated total energy-volume data points.

To analyze the effect of size mismatch on the vacancy formation energy, we rely on the size factor [48,49], which can be calculated as

$$\Omega_{\text{sf}}^M = \frac{N \Delta P}{B}, \quad (3)$$

where N is the number of atoms in the cell, ΔP is the excess pressure induced by substituting an atom of type M in the cell and B is the bulk modulus of the host lattice. The size factor was calculated for Cr and Al in bcc Fe, and for Cr and Ni in fcc Fe, employing the same magnetic configuration and number of atoms as in the full alloy simulations. Since the pressure change in the cell is derived from the derivative of the energy with respect to volume, a stricter convergence criterion was employed, ensuring a convergence to within 0.1 meV/atom. A cutoff energy of 400 eV was used for both systems, along with a $3 \times 3 \times 3$ Monkhorst-Pack grid of k points and a self-consistent electronic loop convergence criterion of 10^{-6} eV. The initial bcc or fcc Fe system was fully relaxed, and a subsequent substitution of an atom was performed. Following the substitution, the system was relaxed again, allowing for only atomic positions to update. The substitution causes an increase or decrease in pressure within the cell, which can be used to calculate the size factor defined in Eq. (3). The size factor was then utilized to investigate the role of the local state of compression or tension near a vacancy, by defining a total size factor as

$$\Omega_{\text{sf}}^{\text{tot}} = \sum \Omega_{\text{sf}}^M N_M, \quad (4)$$

where N_M is the number of solute atoms in the first-nearest-neighbor shell of type M . The total size factor hence represents the first shell compression or tension state. The elastic constants were calculated using DFT perturbation theory as implemented in VASP, from which the bulk modulus was evaluated for both the bcc and the fcc case.

C. Vacancy migration energy

The second set of calculations, aimed to find the vacancy migration energy, was performed by computing the minimum-energy path of the vacancy-atom jump by using the nudged elastic band (NEB) approach implemented in VASP-VTST [50]. The fully relaxed cells from the previous calculation were utilized, introducing vacancies in the initial and final positions along the migration path. The defect lattices were subsequently relaxed, keeping the volume of the cell fixed and allowing atomic positions to update. Three images were created along the migration path, employing the climbing image (CI) algorithm [51]. The CI algorithm forces one of the images in the migration path to be located on the saddle point of the migration barrier. No significant change in the migration barrier was observed when reducing the number of images from 11 to 5.

In order to analyze the influence of the local environment on the migration barrier, the paths were chosen such that the local environment of the migrating atom contained varying quantities of the alloying elements. Specifically, 30 different

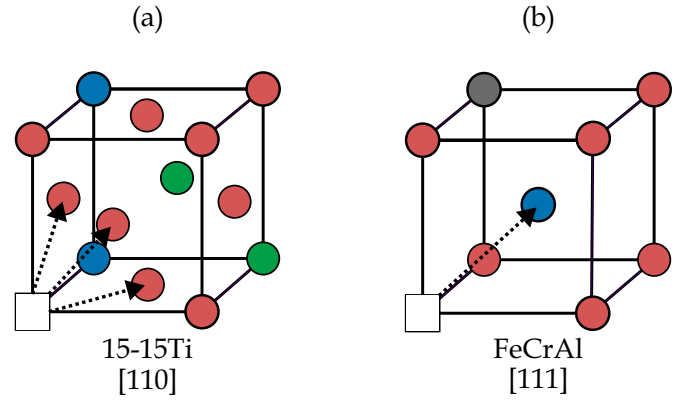


FIG. 1. The most probable migration paths for the two different alloys, these being (a) the [110] direction for 15-15Ti and (b) the [111] direction for FeCrAl. Notably, in 15-15Ti, there are three equivalent migration paths; two of the migration paths are transplanar, and one is in-plane. In the figure, red spheres represent Fe, blue spheres represent Cr, gray spheres represent Al, green spheres represent Ni, and the white square represents a vacancy.

migration paths were created for FeCrAl, and 46 different migration paths were created for 15-15Ti, containing roughly equal distributions of each alloying atom. The migration directions were chosen to be the most probable paths in the two alloys; these being [110] for 15-15Ti and [111] for FeCrAl. An illustration of the migration paths is shown in Fig. 1.

As the migration barriers are not symmetric in alloys due to their disordered nature, the forward and reverse barriers represent unique migration barriers. Therefore, both barriers were utilized in this work, effectively doubling the number of data points for each alloy. The vacancy migration energy can be calculated as

$$E_{\text{m}}^{\text{v}} = E_{\text{b}} - E_{\text{in}}, \quad (5)$$

where E_{m}^{v} is the vacancy migration energy, E_{b} is the saddle-point energy, and E_{in} is the energy of the initial state. It should be noted that if E_{in} is replaced by the energy of the final state, E_{fin} , the reverse barrier energy is found.

D. Effective activation energy of diffusion

To calculate the temperature-dependent effective vacancy formation and migration energies, E_{eff} , the energy barrier that corresponds to the average energy barrier was determined. This quantity can be derived by solving the equation

$$\exp\left(-\frac{E_{\text{eff}}}{k_{\text{B}}T}\right) = \frac{1}{N} \sum w_s \exp\left(-\frac{E_s^{\text{v}}}{k_{\text{B}}T}\right), \quad \text{with } w_s = \frac{\nu_s}{\sum \nu_s}, \quad (6)$$

where E_s^{v} is the formation or migration energy, N is the number of samples in the set, w_s is the weight accounting for the attempt frequency during migration of atoms, ν_s is the species attempt frequency (hence $s = \text{Fe, Cr, Al, or Ni}$), k_{B} is the Boltzmann constant, and T is the temperature. The attempt frequency can only be defined during the migration of a vacancy. Therefore, $w_s = 1$ for the effective vacancy formation energy, and w_s is calculated from the attempt frequencies of

TABLE I. The computed chemical potential of each constituent element of the analyzed alloys.

Element	Chemical potential, μ_x (eV/atom)
Fe	-8.31
Cr	-9.51
Ni	-5.51
Al	-3.74

Fe, Cr, Ni, and Al for the effective vacancy migration energy. The values were taken from impurity diffusion calculations in bcc Fe [52], as no literature values could be found for fcc Fe. However, Eq. (6) is linear in w_s and exponential in E_x^v ; varying v_s by $\pm 30\%$ in 15-15Ti shifts E_{eff} by no more than 0.01 eV, or about 2% of the smallest barrier. Furthermore, the effective energy defined in Eq. (6) does not capture loss of long-range magnetic order, and we hence limit Eq. (6) to below the Curie temperature for the analyzed material. It should be noted that residual entropic variation with temperature remains a second-order approximation within this temperature range. Solving Eq. (6) yields the wanted quantity

$$E_{\text{eff}} = -k_B T \ln \left[\frac{1}{N} \sum w_s \exp \left(-\frac{E_x^v}{k_B T} \right) \right]. \quad (7)$$

Here, E_{eff} represents the total average effective activation energy, such that this energy represents the average energy that will reproduce the ensemble behavior by a single Arrhenius law. Taking the limit as $T \rightarrow 0$ makes E_{eff} approach the minimum value of the evaluated energy, and as $T \rightarrow \infty$, E_{eff} approaches the arithmetic mean, $\langle E_x^v \rangle$, of the energy evaluated. To compute the total activation energy of diffusion, E_a , the effective vacancy formation and migration energies were added together, after individual computation according to Eq. (7) at all temperatures.

III. RESULTS AND DISCUSSION

A. Effective chemical potential and basic properties

The chemical potentials, μ_x , with $x = \text{Fe, Cr, Ni, or Al}$, were calculated using VASP to obtain an estimate of the energy contained within each atom. Table I shows the values of the calculated chemical potentials, with Cr being the most negative, followed by Fe, Ni, and finally Al. The chemical potential can be estimated through numerous approaches, such as the Widom substitution [28], but was here approximated by accurate relaxations of perfect cells of the alloying elements. It should be noted that for alloys, the chemical potential is different depending on the alloy composition. Here, we used the simplest case as the chemical potential will only shift the vacancy formation energy by a constant amount, meaning that as long as the same value is used throughout all calculations, the trends will be independent of the chemical potential applied.

The spin configurations chosen for this study were [100] AFM for 15-15Ti, and FM with respect to the Fe atoms for FeCrAl, with Cr in local AFM configuration. Figure 2 shows the magnetic moments of Cr, Ni, and Al in the respective alloys versus the sum of the magnetic moments of the Fe first nearest neighbors. From the figures, the magnetic ground

TABLE II. Bulk modulus and atomic size factors for fcc and bcc Fe-based systems.

Property	fcc	bcc
Bulk modulus, GGA (GPa)	196.7	195.5
Size factor (Cr)	-0.12	0.19
Size factor (Ni/Al)	-0.18	0.20

state of each configuration can be determined. The trends show that in 15-15Ti, Cr couples antiferromagnetically to Fe first nearest neighbors, with magnetic moments between $1.5 \mu_B$ and $-1.5 \mu_B$. On the other hand, Ni couples ferromagnetically to Fe first nearest neighbors and exhibits magnetic moments between $0.4 \mu_B$ and $-0.4 \mu_B$. The results are similar to previous studies [17], showing that Ni is generally more magnetically compliant, and Cr can in some instances get magnetically frustrated. Three outliers can be identified in Fig. 2(a), where Cr atoms do not couple antiferromagnetically to Fe first nearest neighbors. Interestingly, the Cr moments create two distinct populations in Fig. 2(a): one with positive and with one negative magnetic moment. The behavior is observed to be different from Figs. 2(b)–2(d), as the atoms exhibit more continuous distributions of magnetic moments.

In FeCrAl, Cr couples antiferromagnetically to Fe first nearest neighbors, with magnetic moments between $-0.25 \mu_B$ and $-2 \mu_B$. Al shows weak antiferromagnetic magnetization, with moments between $-0.04 \mu_B$ and $-0.08 \mu_B$. The quenching of some magnetic moments can be attributed to the local environment, specifically to Al-rich neighborhoods.

Figure 3 shows the distribution of local magnetic moments versus the Voronoi polyhedral cell volumes for all constituent atoms and reveals two distinct populations of Fe and Cr atoms in 15-15Ti, with atomic volumes ranging from $10.7 \text{ \AA}^3$ to $11.4 \text{ \AA}^3$. Ni shows a more uniform distribution, agglomerating around $0 \mu_B$. In Fig. 2(a), there are three Cr atoms that do not couple antiferromagnetically to neighboring Fe, and the reason can be seen in Fig. 3(a). The two Cr atoms with the largest atomic volumes are also the ones that develop positive magnetic moments and deviate from the expected antiferromagnetic coupling. This magnetic frustration leads to an expansion of their atomic volumes. In contrast, the third Cr atom that also breaks the antiferromagnetic trend, but retains a small negative magnetic moment, is located in a Ni-rich environment, with four Ni neighbors. The strong Ni-Cr interactions locally quench the magnetic moment of the Cr atom, resulting in an atomic volume and magnetic moment comparable to that of nearby Ni atoms.

Table II shows the calculated bulk moduli and size factors for each system, showing that within the PAW-GGA exchange-correlation functional, the bulk moduli for FM bcc Fe and AFM [100] fcc Fe are on similar orders of magnitude. It should be noted that, without austenitic stabilizers present in the matrix, such as Ni, the ground state of AFM [100] fcc Fe is slightly tetragonal, with the c lattice vector being about 5% longer than the other lattice vectors. Nevertheless, the bulk moduli could successfully be calculated and are on similar magnitudes as previous studies [53]. The size factors were calculated according to Eq. (3), and reveal that in the bcc

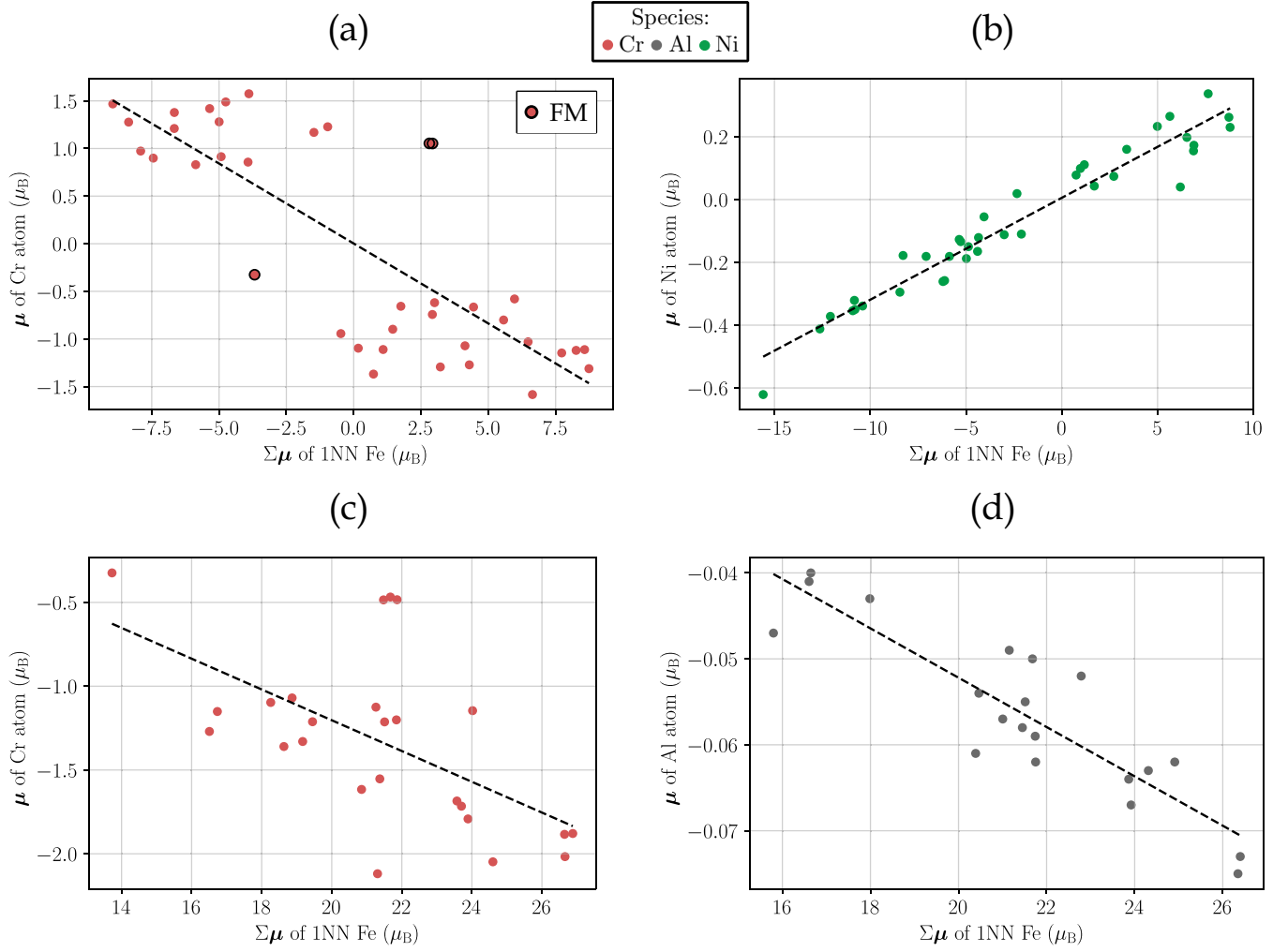


FIG. 2. The sum of magnetic moments carried by Fe first nearest neighbors versus the magnitude of moments carried by (a) Cr and (b) Ni in 15-15Ti, and (c) Cr and (d) Al in FeCrAl. 15-15Ti was initialized in the [100] AFM state, while FeCrAl was initialized in the AFM state with respect to Fe and Cr atoms. The Cr atoms that couple ferromagnetically to the surrounding Fe atoms in 15-15Ti have been marked with a black circle.

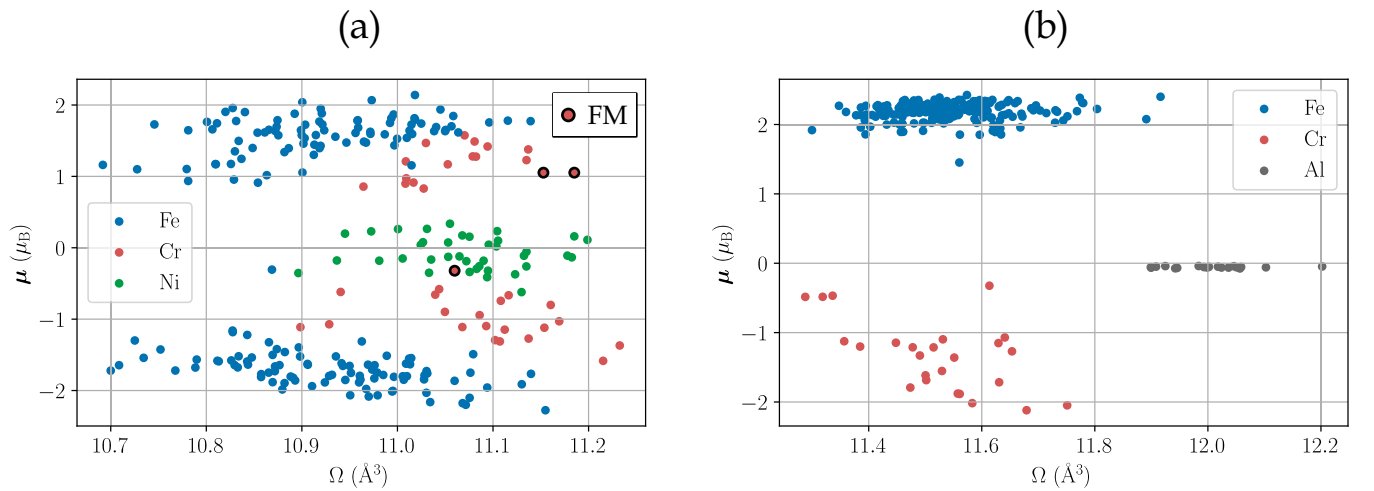


FIG. 3. The distribution of local magnetic moments in relation to the local atomic volume for (a) 15-15Ti and (b) FeCrAl. The distributions reveal two separate populations of Fe and Cr atoms in 15-15Ti, as expected in an AFM alloy, while Fe and Cr show AFM coupling in FeCrAl. The Cr atoms that couple ferromagnetically to the surrounding Fe atoms in 15-15Ti have been marked with a black circle.

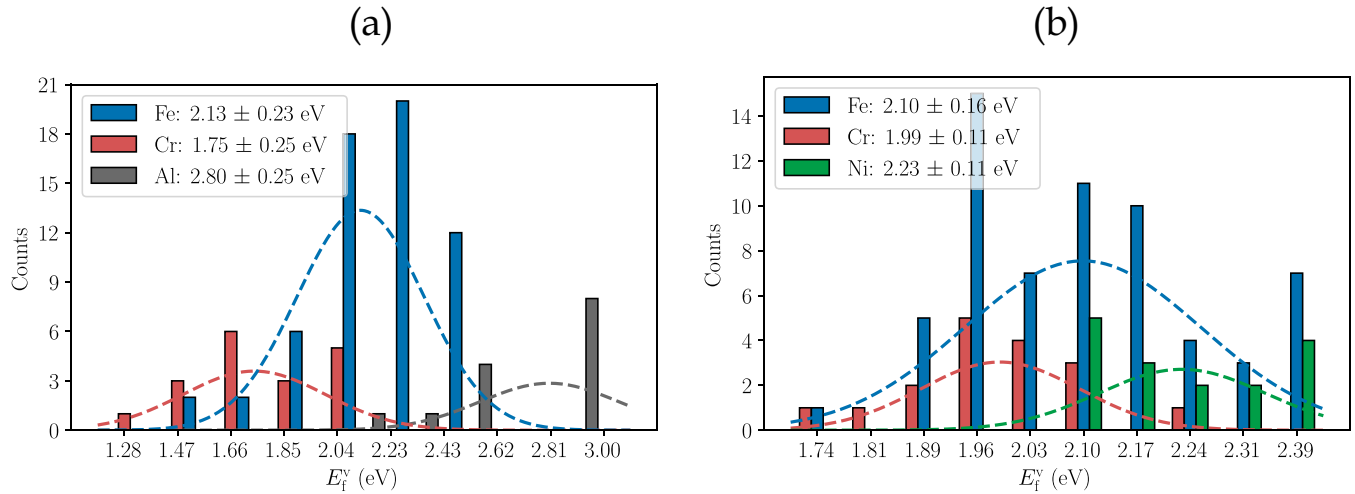


FIG. 4. Distributions of the vacancy formation energy for (a) 15-15Ti and (b) FeCrAl, along with Gaussian fits to each alloying element fitted with the calculated mean and standard deviation.

lattice, both Cr and Al are oversized, with Al being slightly larger than Cr. On the contrary, in the fcc lattice, both Cr and Ni are undersized, with Ni being smaller than Cr. The Cr size factor in bcc Fe can be compared to previous studies, and shows excellent agreement [49,54].

B. Vacancy formation energy

Figure 4 shows the distribution of the calculated vacancy formation energies from VASP, for each alloying element in the respective alloys. To analyze if the samples stem from a normal distribution, the Shapiro-Wilk test for normality was performed for the constituent elements of each alloy, yielding the Shapiro p-value [55]. For 15-15Ti, the p-values were found to be 0.1, 0.7, and 0.1 for Fe, Cr, and Ni, respectively. As the values are larger than 0.05, the individual elements should follow a normal distribution. Interestingly, Ni has a flatter distribution and spans only about 0.3 eV as compared to Fe and Cr spanning 0.7 eV and 0.5 eV, respectively. The flatter, and narrower distribution could be due to the magnetic compliance of Ni, meaning that Ni is not as influenced by local environment as compared to Fe and Cr in 15-15Ti. In FeCrAl, the distributions of Fe, Cr and Al show p-values of 0.001, 0.5, and 0.1, respectively, meaning that the Fe samples do not stem from a normal distribution. Instead, the vacancy formation energies mostly fall within the vacancy formation energy of pure bcc Fe of ~ 2.2 eV [56]. This is expected because Cr and Al are present in relatively low concentrations, so the local chemical environment around most Fe sites remains Fe rich and therefore Fe-like. Additionally, for Al, the distribution is also skewed towards higher vacancy formation energies due to Al not being intrinsically stable in the bcc structure. When incorporated in the Fe-Cr matrix, Al atoms experience an energetically unfavorable environment, which increases the cost of vacancy formation.

The average value of the relaxed and unrelaxed vacancy formation energies was calculated as an arithmetic mean of all data points generated with VASP. Table III shows the calculated values from VASP for both alloys, along with the vacancy formation energy as calculated by EMT-CPA and the de-

rived vacancy migration energies. Uncertainties correspond to one standard deviation of the generated dataset. The absolute values of the average vacancy formation energy from VASP were found to be 2.10 eV and 2.15 eV for 15-15Ti and FeCrAl, respectively, in the relaxed case. The unrelaxed vacancy formation energy was found to be 2.21 eV and 2.40 eV for 15-15Ti and FeCrAl, respectively, showing that the effect of relaxing the cell is between 0.1 eV and 0.25 eV. The relaxed values can be compared to previous studies, which show that for an FeCrNi alloy containing 10 at.% Ni and 20 at.% Cr the mean value of the vacancy formation energy is 0.15 eV lower [17]. The increased mean vacancy formation energy can be attributed to the increasing Ni content. As seen in Table III, Ni has an average formation energy of 2.23 eV, while Cr has an average formation energy of 1.99 eV. Increasing the Ni content, and reducing the Cr content will cause the average vacancy formation energy to increase.

Figure 5 shows the vacancy-formation energy-landscape as calculated by EMT-CPA. In 15-15Ti, the smallest vacancy formation energy stems from the greatest concentration of Ni, and the smallest concentration of Cr. In contrast, FeCrAl has smaller vacancy formation energy at the greatest concentration of Cr. In the figure, some points are marked for comparison. The first points that are marked are the compositions analyzed in this study, namely 15 at.% Cr and 15 at.% Ni in Figs. 5(a) and 5(b), and 10 at.% Cr and 8 at.% Al in Fig. 5(c), showing that the unrelaxed vacancy formation energy from EMT-CPA is 2.13 eV and 2.09 eV, in the PM state and AFM state for 15-15Ti, respectively, and 2.41 eV for FeCrAl. Comparing these values to the average vacancy formation energy calculated from VASP shown in Table III shows that the vacancy formation energy is in agreement between both methods. The other marked points, at 20 at.% Cr and 10 at.% Ni, correspond to the composition analyzed in a previous study [17]. The study found an average vacancy formation energy in that alloy of 1.96 eV; adding 0.1 eV to account for relaxation and assuming a standard deviation of similar order of magnitude as this study, we find that the EMT-CPA calculations are in agreement with this study as well. Moreover, the EMT-CPA calculations highlight the impor-

TABLE III. Vacancy formation energies, E_f^v , and migration energies, E_m^v , for the 15-15Ti and FeCrAl alloys. The unrelaxed vacancy formation energy is only shown for the total average as it is utilized for comparison with EMTO-CPA. Uncertainties quoted correspond to one standard deviation.

Method	System	Species	VASP			EMTO-CPA
			E_m^v (eV)	$E_{f,rel}^v$ (eV)	$E_{f,unrel}^v$ (eV)	
15-15Ti		Fe	0.95 ± 0.13	2.10 ± 0.16	2.21 ± 0.18	2.13 (PM)/ 2.09 (AFM)
		Cr	0.80 ± 0.15	1.99 ± 0.11		
		Ni	1.22 ± 0.13	2.23 ± 0.11		
		Mean	0.99 ± 0.22	2.10 ± 0.16		
FeCrAl		Fe	0.58 ± 0.22	2.13 ± 0.23	2.40 ± 0.37	2.41
		Cr	0.63 ± 0.23	1.75 ± 0.25		
		Al	0.48 ± 0.25	2.80 ± 0.25		
		Mean	0.56 ± 0.24	2.15 ± 0.39		

tance of the choice of magnetic state for the vacancy formation energy calculations. While the vacancy formation energies at the analyzed composition are within 0.05 eV of each other, and both fall within the error margins of the VASP calculation, the vacancy-formation energy landscape is different. For the PM state, shown in Fig. 5(a), the landscape has a minimum at

low Cr content, and high Ni content and a maximum at high Cr content and low Ni content. The same trend can be seen in the AFM state, shown in Fig. 5(b), though slightly more subtle, as the minimum is not as clear at high Ni content. The maximum point at low Ni and high Cr remains, consistent with the PM state. To elucidate the mechanisms of vacancy formation in

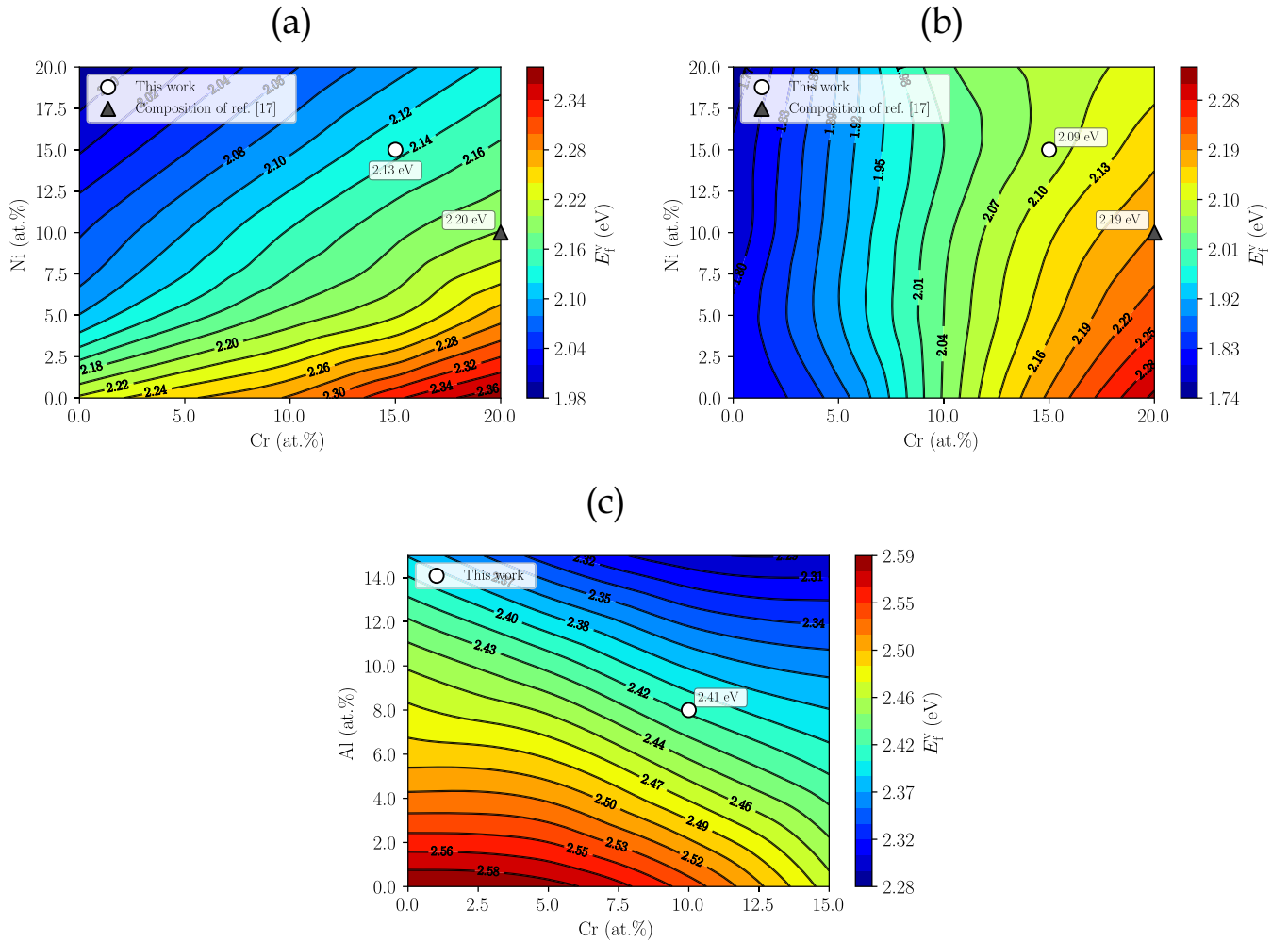


FIG. 5. The vacancy-formation energy-landscape, as calculated by EMTO-CPA, for (a) 15-15Ti in the PM state, (b) 15-15Ti in the AFM state, and (c) FeCrAl. The marked points correspond to the concentrations of the alloys computed with VASP, as well as the concentration analyzed in a previous study [17]. It should be noted that all quoted values marked in the figure are computed by EMTO-CPA.

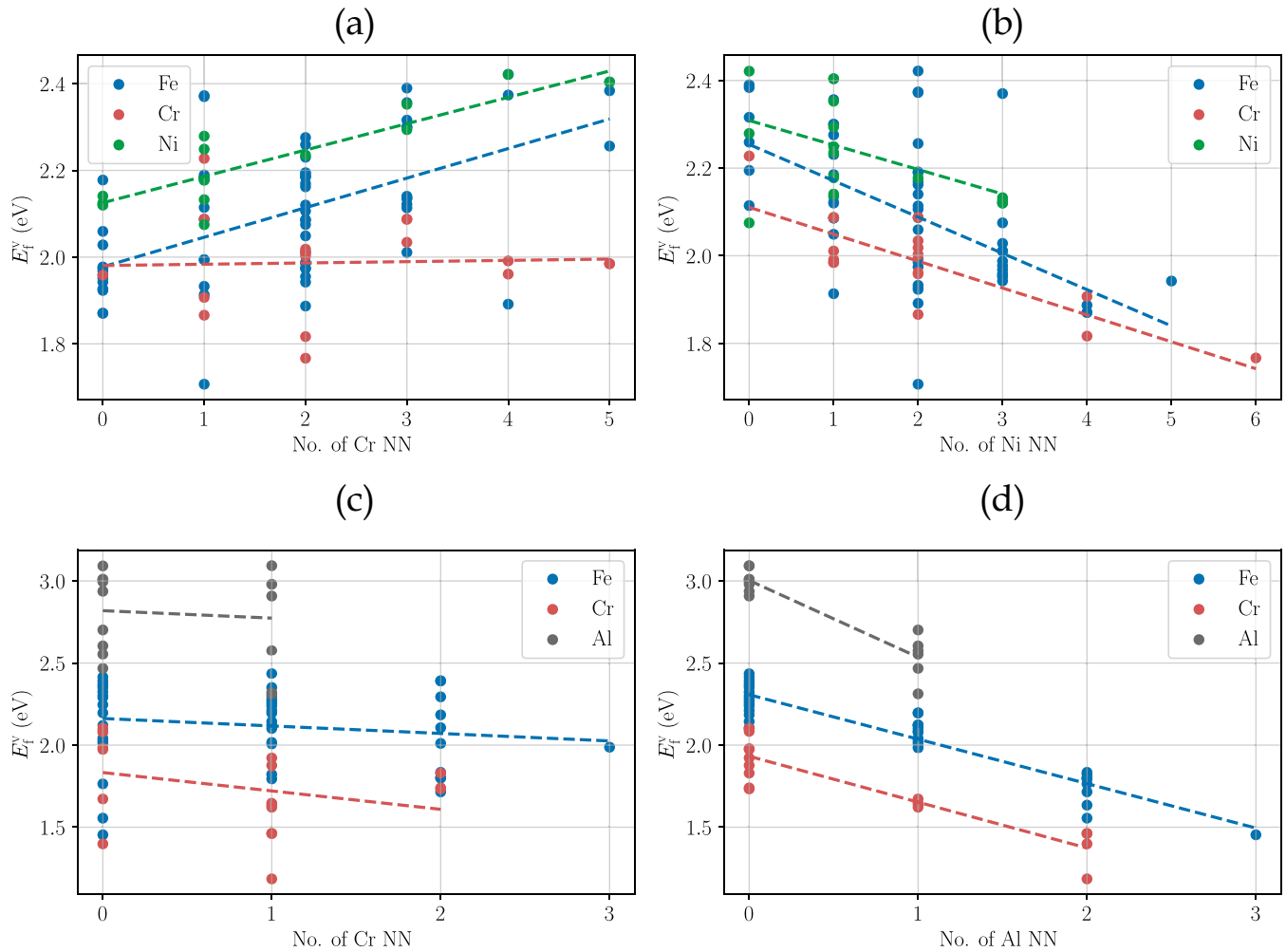


FIG. 6. Vacancy formation energy distributions as a function of local chemical environment for 15-15Ti and FeCrAl. (a) and (b) correspond to the austenitic 15-15Ti alloy, while (c) and (d) show results for the ferritic FeCrAl alloy.

the alloys, Fig. 6 shows the vacancy formation energy as a function of the number of first nearest neighbors of Cr, Ni, or Al, revealing the effect of local environments on the vacancy formation energy. The local environments' effect on the vacancy formation energy shows that increasing the number of Cr first nearest neighbors increases the vacancy formation energy in 15-15Ti and reduces the vacancy formation energy in FeCrAl. Both Ni and Al present in the local environment reduce the vacancy formation energy. These results are in agreement with the trends shown in Fig. 5, and the average values of the vacancy formation energy of both methods fall within the error margin of the VASP calculations.

The results shown in Fig. 6 agree with previous studies [17,26], showing that Ni tends to bind to vacancies and the Cr-vacancy interaction is repulsive in austenitic alloys. The binding of Ni and vacancies can be attributed to the magnetic stability of Ni atoms in the austenitic alloy, and the increased density of states (DOS) at the Fermi energy caused by localization of $3d$ electrons [57]. Conversely, Cr atoms in the austenitic alloy are magnetically frustrated due to their near half-filled $3d$ shells. The reduced coordination caused by the vacancy locally increases the magnetic moments and thereby increases the magnetic penalty. In

FeCrAl, the Cr-vacancy interaction is slightly attractive [56], reducing the vacancy formation energy by about 0.05 eV as the number of first-nearest-neighbor Cr atoms increases near the vacancy, due to the reduced magnetic frustration of Cr as a vacancy is introduced in the first-nearest-neighboring atoms. As the concentration of Cr near a vacancy increases to more than three atoms, the vacancy formation energy will likely start increasing due to competing magnetic moments and further magnetic frustration due to the Cr-Cr interactions as previously found [40]. Similarly, the vacancy formation energy is strongly correlated with Al first nearest neighbors, shown in Fig. 6(d), decreasing by up to 0.5 eV as the number of first nearest neighbors of Al increases. This trend originates from the significant atomic-size mismatch between Al and Fe/Cr. The presence of Al introduces local strain on the lattice, which is relieved when a vacancy is formed in its vicinity, thereby lowering the vacancy formation energy [58,59].

To further strengthen the size argument in the ferritic alloy, we calculate the total size factor according to Eq. (4) and perform a similar trend analysis as described previously. The results are shown in Fig. 7, and reveal expected trends: for the austenitic 15-15Ti, the undersized atoms do not heavily

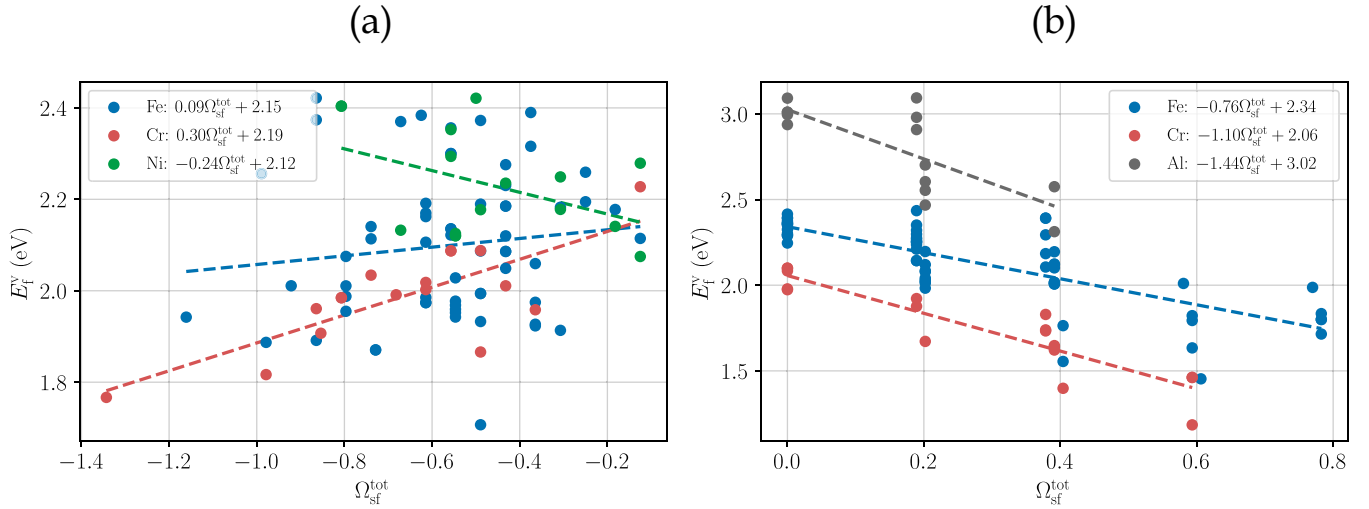


FIG. 7. Vacancy formation energy distributions as a function of the total size factor defined in Eq. (4) for (a) 15-15Ti and (b) FeCrAl, showing that the dominating effect in FeCrAl is the size mismatch of the alloying elements, while for 15-15Ti the magnetic effects dominate.

influence the vacancy formation energy, as it is controlled by the magnetic stability of Ni and the magnetic frustration caused by Cr in the fcc lattice. Conversely, for the ferritic FeCrAl, the trends look very similar to Fig. 6, confirming that the dominating effect for vacancy formation in FeCrAl is the size mismatch between Fe and the alloying atoms, specifically Al as will be further described in the following section.

From the trends seen in Fig. 7(b), a model can be formulated from basic properties of the alloy, predicting the vacancy formation energies by exclusively analyzing the atomic size mismatch between the host lattice and the solute atoms. The optimal slope between the vacancy formation energy and the total size index can be calculated to be $0.865 \text{ eV}/\Omega_{sf}^{tot}$. By defining the intersection of the line with the y axis for the three different atoms as the average vacancy formation energy of each alloying atom with exclusively Fe first nearest neighbors, $\bar{E}_f^v(0)$, we can propose a simple, first-order approximation of the vacancy formation energy in the ferritic FeCrAl alloy. The results are shown in Fig. 8.

Remarkably, the R^2 value of the fit is 0.854, indicating that employing the total size factor as a descriptor can accurately predict the vacancy formation energy. Hence, in this ferritic FeCrAl alloy, we only need to calculate the size factors of the alloying elements and the vacancy formation energy of a few sites, containing exclusively Fe first nearest neighbors, to extrapolate to any local environment with sound accuracy. The intersections with the y axis in Fig. 7(b) could also be defined from fundamental vacancy formation energies of binary alloys, or pure metals. We calculated the vacancy formation energy of Fe in pure bcc Fe, Cr in bcc Fe-10Cr, and Al in Fe-8Al to be 2.18 eV, 1.91 eV, and 2.81 eV, respectively. Comparing the calculated values to the intersections presented in Fig. 7(b) indicates a systematic underestimation of about 0.1 eV, meaning that the intersections with the y axis could also be derived from fundamental vacancy formation energies.

C. Vacancy migration energy

The vacancy migration energies in the two ternary alloys, 15-15Ti and FeCrAl, were evaluated for all relevant atom-vacancy exchanges using VASP. Table III shows the total averaged vacancy migration energy across all calculations. Rather than a single characteristic barrier, the migration energy shows pronounced variations with the local environment as the energy is dependent on the initial and final environment, as well as the atomic species taking part in the exchange. We find that in 15-15Ti, the Ni-vacancy exchange has the largest vacancy migration energy, followed by the Fe-vacancy and the Cr-vacancy exchanges, with standard deviations on the order of 0.1 eV. In FeCrAl, the largest vacancy migration energy is the Cr-vacancy exchange, followed by the Fe-vacancy exchange and lastly the Al-vacancy exchange, with standard deviations on the order of 0.2 eV.

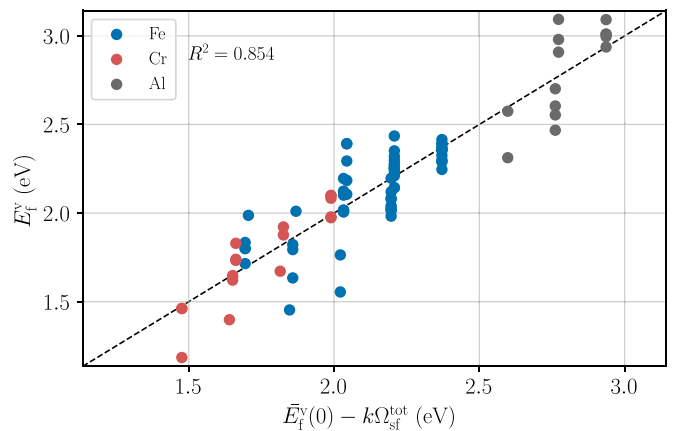


FIG. 8. Comparison between calculated vacancy formation energies and the proposed model, employing a slope of $0.865 \text{ eV}/\Omega_{sf}^{tot}$. The R^2 value of the model is 0.854, indicating that exclusively using the total size factor as a descriptor can successfully predict the vacancy formation energy in the alloy.

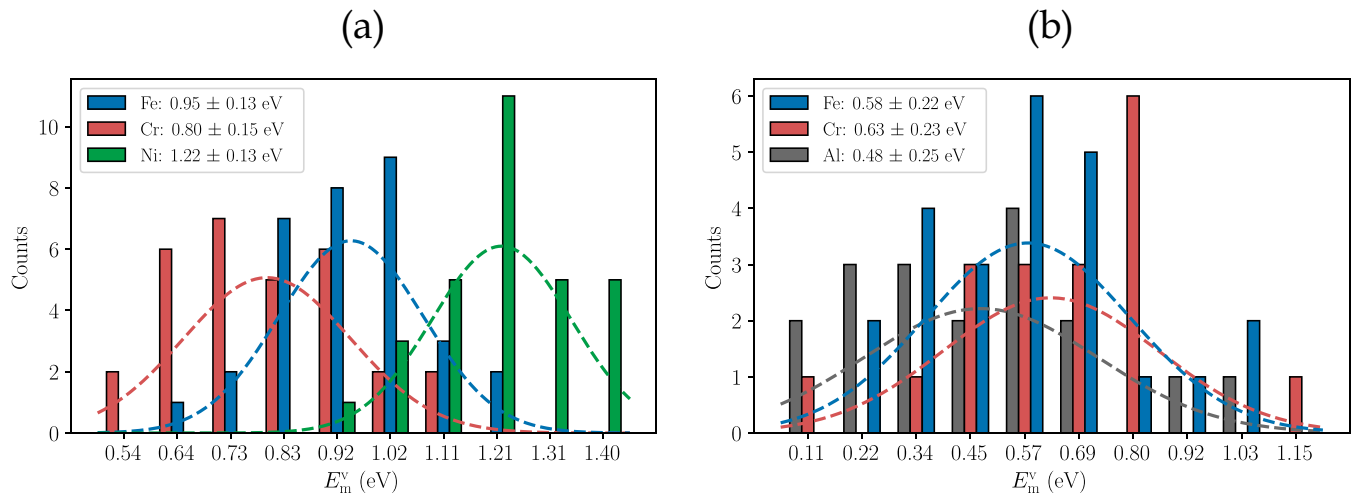


FIG. 9. Distributions of the vacancy migration energy for (a) 15-15Ti, and (b) FeCrAl, along with Gaussian fits to each alloying element fitted with the calculated mean and standard deviation.

Figure 9 shows the distributions of vacancy migration energies, and shows that the distributions are more narrow in 15-15Ti and broader in FeCrAl. The Gaussian-like distributions shown in Fig. 9 indicate that, for both alloys, there is not a single vacancy migration energy, but a wide distribution of local environments, each yielding a different barrier energy. The distributions also indicate that the migration of vacancies in 15-15Ti is not dominated by a single mechanism, meaning that local environment, atomic species and magnetic effects all play important roles in the atom-vacancy exchange.

The situation is slightly more complicated for FeCrAl, shown in Fig. 9(b), as all the distributions show large standard deviations (up to 52% of the mean). Specifically, Fe- and Cr-vacancy exchange seem to have a fraction of difficult jumps, as they are slightly tail heavy towards high vacancy migration energies. Conversely, the Al-vacancy exchange has the lowest mean vacancy migration energy, and is very tail heavy towards lower energies, suggesting that there is a mechanism making the Al-vacancy exchange easier. To elucidate the mechanisms, we present the distributions of each atom-vacancy migration barrier independently, as functions of the strongest correlation found across the generated dataset in Fig. 10.

The vacancy migration energies for both the Fe- and Cr-vacancy exchange in 15-15Ti were found to be positively correlated with the total change in magnetization of the cell as seen in Fig. 10, suggesting a similar mechanism in the vacancy-atom exchange. The migration barriers are hence primarily controlled by the local magnetic environment, as both Fe and Cr carry large magnetic moments that might undergo large perturbations as the atom migrates [22]. For the Ni-vacancy exchange, a positive correlation was found with the change in Ni atoms between the initial and final states of the vacancy, meaning that migrating to a site with more Ni atoms costs more energy in the system, indicating that Ni tends to disperse in the alloy.

In FeCrAl, Al was found to have the greatest influence on the vacancy migration energy, as shown in Fig. 10. The strongest correlations involve the change in Al nearest neighbors for the Fe- and Cr-vacancy exchange, and the number of Al first nearest neighbors for the Al-vacancy exchange.

From the derived trends, we can state that the dominating effect on the vacancy migration energy in FeCrAl alloys will be the solute-vacancy interaction along with the size mismatch of Al in the lattice. As seen in Figs. 10(b) and 10(d), migrating to sites with fewer Al atoms is more energetically favorable. The reason for this effect can be split into two parts: the Al-vacancy binding energy, and the size mismatch of Al in the lattice. The Al-vacancy binding energy has been found to be positive, with an absolute value of 0.288 eV, about five times larger than the Cr-vacancy binding energy [19,56]. This means that in the case where Fe or Cr atoms migrate to a site where a vacancy is bound to many Al atoms, the migration energy is large as many Al-vacancy bonds have to be broken. On the contrary, when the vacancy migrates from an Al-poor to an Al-rich environment, the migration energy is small. Similarly, for migrating Al, when the final position of the vacancy has more Al nearest neighbors, the vacancy migration energy decreases.

As shown in Fig. 7, size mismatch dominates the vacancy formation energy, which is further enhanced during the migration of atoms in the lattice, specifically for Al. As Al exhibits an *sp* electronic structure, and low magnetic moments, the bonds are forced to hybridize with the *d* orbitals of the host Fe atoms during migration [60], screening the lattice strain less efficiently. Additionally, as seen in Fig. 3(b), Al remains genuinely oversized in the concentrated alloy, whereas Cr can partially accommodate its lattice mismatch through its magnetic degree of freedom, which is unavailable for Al. Since the oversizing of Al is not relieved by any such magnetic relaxation, the resulting perturbation of Al first nearest neighbors dominates the vacancy migration energy. In contrast, Cr is more efficiently incorporated into the concentrated alloy, since Cr clustering collapses the magnetic moments and relaxes the lattice distortion around it.

The results shown in Fig. 10 indicate that for the Fe- and Cr-vacancy exchange in 15-15Ti, vacancy migration energies are not only governed by local atomic environment, but also by magnetic reconfiguration in accordance with previous findings for ferritic FeCr alloys [22]. As shown in Fig. 2(a), Cr tends to couple antiferromagnetically to Fe

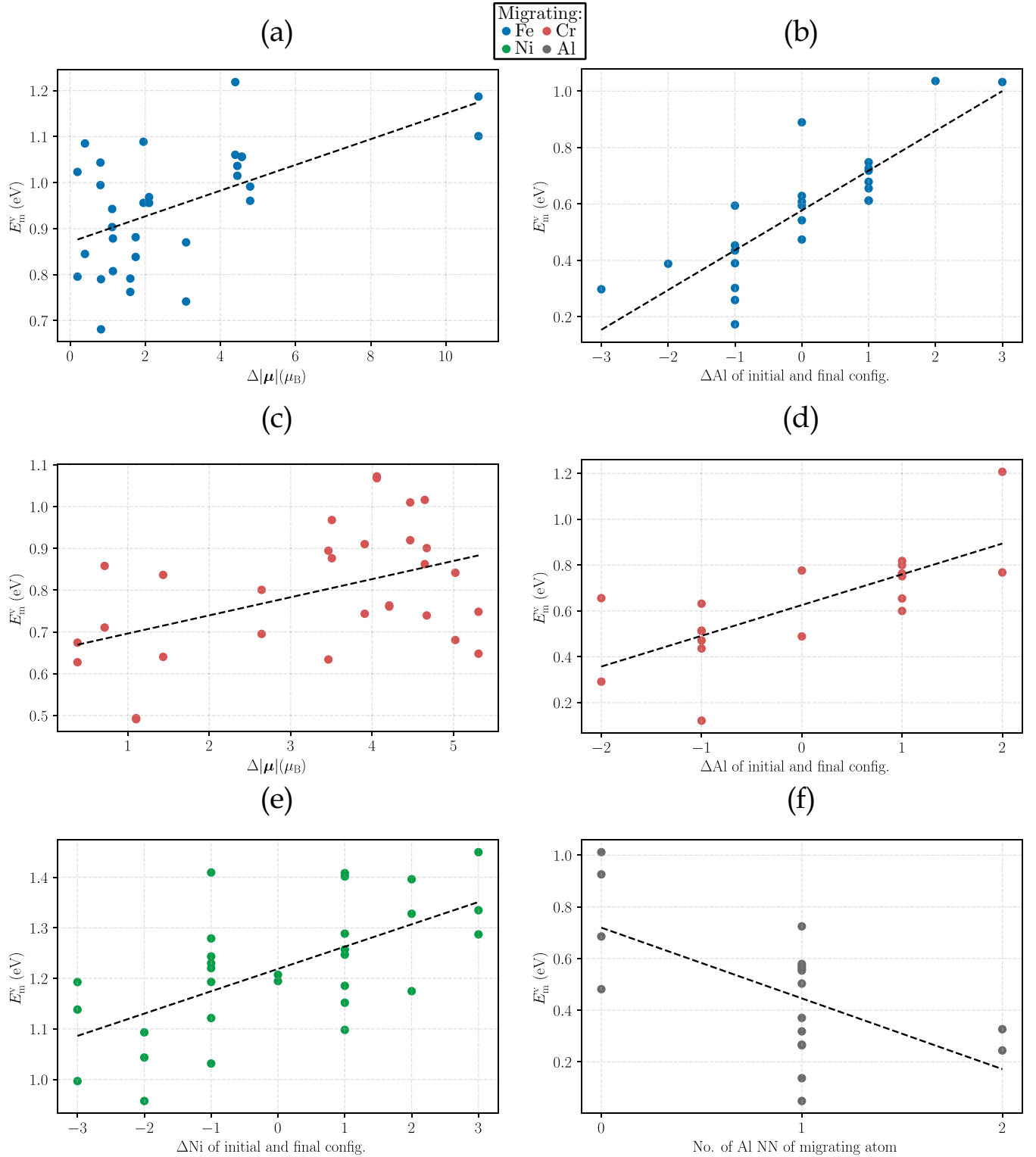


FIG. 10. The vacancy migration energy as functions of the strongest correlations found in each data set for (a) Fe, (c) Cr, and (e) Ni in 15-15Ti and (b) Fe, (d) Cr, and (f) Al in FeCrAl. The change in Al or Ni atoms of the initial and final configuration represents the difference of first-nearest-neighbor Al or Ni atoms of the migrating atom. Hence, if this value is equal to, for example, two, the atom migrates to a site with two more Al or Ni atoms than the initial configuration.

first-nearest-neighbor atoms. At the same time, Cr also tends to couple antiferromagnetically to first-nearest-neighbor Cr atoms, which leads to competing orientation states. This can lead to magnetic frustration of the Cr atoms, which are

forced to occupy a higher-energy magnetic state, consequently increasing the energy of the system. If a Cr or Fe atom moves into a site that causes greater magnetic frustration, a larger magnetic reconfiguration needs to be made. This magnetic

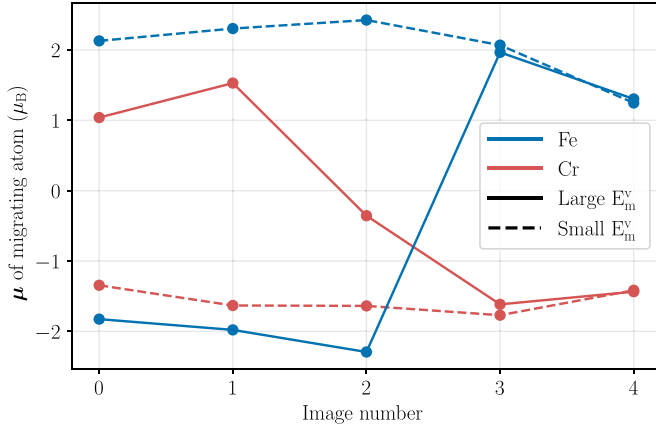


FIG. 11. Local magnetic moment of Fe and Cr in 15-15Ti for paths with large and small vacancy migration energies, revealing that when the vacancy migration energy is large, the migrating atom undergoes a spin flip.

reconfiguration can be seen as a large change in total magnetization of the cell and explains why the magnitude of the change in magnetic moment is correlated with the vacancy migration energy.

Figure 11 shows the local magnetic moments of migrating Fe and Cr atoms for two types of barriers along the migration path. The local magnetic moment is shown for two migration paths for each migrating atom corresponding to one large and one small vacancy migration energy. The difference is clear: when the atom undergoes a spin flip during the migration, the vacancy migration energy is large. The migration paths where spin flips occurred were generally not in-plane transitions, but rather a transplanar migration, thus forcing the atom to undergo a spin flip. The flipping of spin and transplanar migration increases the vacancy migration energy, as the alloy not only needs to account for local atomic environment, but also for the local magnetic environment.

As previously seen in Ref. [22], the magnetic interplay between Fe and Cr atoms is important to understand and to accurately describe the migration of atoms in antiferromagnetic alloys. No strong correlation between vacancy migration energies and change in magnetic moment was found for the Ni-vacancy exchange or any of the atom-vacancy exchanges in FeCrAl. Ni, being magnetically stable in the austenitic alloy, is thus affected more by local atomic environment than the magnetic environment. A similar argument can be made for all atoms in FeCrAl; the size-mismatch of Al with the other alloying elements is truly the dominating factor, and suppresses the magnetic effect on the vacancy migration energy.

D. Effective activation energy of diffusion

To calculate the effective activation energy, Eq. (7) was employed with the dataset generated in Secs. III B and III C. In addition, the total effective activation energy of diffusion, E_a , was calculated by summing the contributions from the vacancy formation energy and the vacancy migration energy. The results are shown in Fig. 12 for both alloys between 0 K and 900 K, as to not allow for excess contributions from vibrational entropy, or loss of long-range magnetic order. The limit was set to the Curie temperature of a similar FeCrAl alloy, containing 10 wt.% Cr and 6 wt.% Al [61].

In both systems, the effective vacancy formation and migration energies are increasing monotonically, approaching the arithmetic mean values (dashed lines) in the high-temperature limit. At low temperatures, the effective energies are significantly reduced, since only the lowest-energy configurations accessible to both systems. When temperature increases, more and more higher-energy states become available, gradually increasing the effective energies. The stronger temperature dependence seen in Fig. 12(a) as compared to Fig. 12(b) can be attributed to the broader and generally

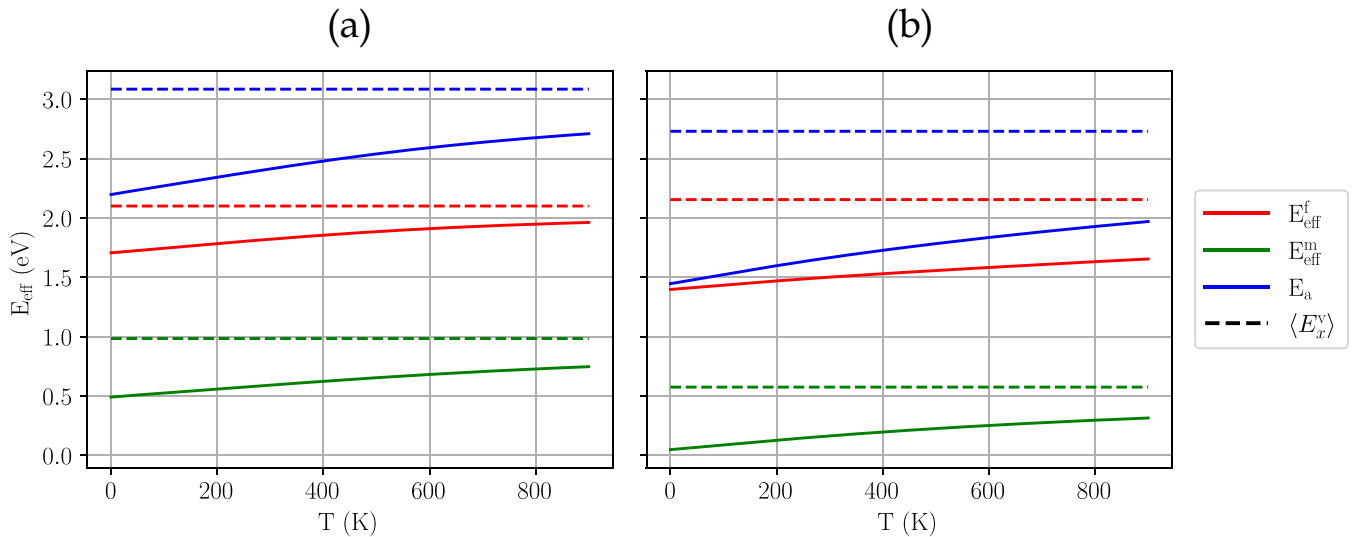


FIG. 12. The effective energy barriers as functions of temperature for (a) 15-15Ti, and (b) FeCrAl. In the figure, the dashed lines correspond to the arithmetic mean of either the vacancy formation energy or the vacancy migration energy.

larger underlying energy distribution as seen in Figs. 4 and 9. The effects of the large atomic-size mismatch of Al with the rest of the matrix in FeCrAl also affect the distributions, as many low-energy vacancy migration barriers exist, which skew the effective migration energy to near-zero values as the temperature tends to 0.

The calculated activation energies for both alloys can be compared to the activation energies for several similar alloy compositions. The austenitic 15-15Ti and the ferritic FeCrAl have, in this study, calculated activation energies of 3.09 eV and 2.72 eV, respectively, in the high-temperature limit. The austenitic 15-15Ti can be compared to experiments performed on γ -Fe alloys [62], which found that adding about 8 wt.% Cr to the Fe increases the self-diffusion activation energy from 3.06 eV to 3.53 eV. Conversely, adding 15 wt.% Ni to the Fe reduces the self-diffusion activation energy to 2.43 eV. The trends are hence similar to what was found in this study, and qualitatively correct. No quantitative comparison can be made as there are no literature values for the exact alloy composition studied here.

The ferritic FeCrAl can be compared to existing literature values for vacancy formation and migration energies in bcc Fe [63], showing that the vacancy formation energy is 2.18 eV and the vacancy migration energy is 0.73 eV in this case. This yields an activation energy for diffusion of 2.91 eV. The effect of alloying Fe with Cr and Al decreases the activation energy of diffusion by 6.5%. To isolate the effect of the different components in the alloy, the same value can be compared to the self-diffusion activation energy of Fe in Fe-12Cr, which has been found to be 2.54 eV [64]. This implies that Cr will enable, while Al will inhibit, vacancy diffusion in the alloy.

Such effective vacancy formation and migration energies can be utilized to predict temperature-variable shifts to create similar microstructural evolution for neutron and ion irradiation, enabling accelerated analysis of irradiation-induced effects for alloys [65], effectively reducing the time for qualification substantially.

IV. CONCLUSION

In this paper, we have determined the vacancy formation energy and the vacancy migration energy for two reactor-relevant materials, namely 15-15Ti and FeCrAl, by employing DFT calculations of the major alloying elements of the two materials. The magnetic ground state of each alloy was found by analyzing the coupling of each alloying atom to the Fe matrix. We find that Cr couples antiferromagnetically to Fe environments in both 15-15Ti and FeCrAl. Ni, present in 15-15Ti, shows weak ferromagnetic coupling to neighboring Fe atoms, while Al, present in FeCrAl, shows weak antiferromagnetic coupling to neighboring Fe atoms.

We show that the vacancy formation energy can be correlated with the local environment of the formed vacancy, in agreement when utilizing VASP and EMTO-CPA. We therefore conclude that using EMTO-CPA is an efficient way of sampling the compositional dependence of the vacancy formation energies. We further conclude that relaxation of the vacancy

formation energy is on the order of 0.1 eV. Further work could be done to ensure that the effect of relaxation is uniform across various alloy compositions. Additionally, it was found that defining a total size factor, describing the total size mismatch between the removed atom and its neighbors, reveals the same trends as the chemical environment of the vacancy formation energy of FeCrAl, meaning that the oversizing of Cr and Al in the matrix explains the observed trends. Conversely, no correlation could be found between total size factor and vacancy formation energy of 15-15Ti, due to the dominating magnetic effects. Based on the correlations derived from the total size factor, we propose a model that can soundly predict the vacancy formation energies in any environment, utilizing only a few calculations of the vacancy formation energy.

The vacancy migration energy was found to be highly influenced by both the local chemical, and magnetic environment. In 15-15Ti, the magnetic interplay between Fe and Cr dominates, causing the vacancy migration energy for both the Fe- and Cr-vacancy exchange to be positively correlated with the total change in magnetization. The cause of the correlation was found to be forced spin flips through transplanar migration of Fe or Cr atoms. Ni was found to be magnetically stable in the alloy, and showed tendencies to disperse in the matrix. In FeCrAl, the dominating effect was concluded to be the size mismatch of Al atoms with the other alloying elements.

From the calculated vacancy formation and migration energies, we calculated thermodynamically averaged quantities, yielding temperature-dependent effective activation energies for the diffusion of vacancies. The values can be seen as an average formation or migration energy at the specific temperature, accounting for the rate-controlled nature of such quantities. In future work, the derived quantities will be used to predict temperature-variable shifts to enable comparable microstructural evolution between ion and neutron irradiated samples, accelerating the qualification of advanced austenitic and ferritic alloys.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support by the Swedish Energy Agency for the Nuclear Materials Platform (NuMaP) under Project No. P2023-01348, as well as the Swedish Foundation for Strategic Research (Stiftelsen för Strategisk Forskning, SSF) under Grant No. ARC19-0043 (the SUNRISE center). The authors also acknowledge EUROfusion for providing access to the Pitagora supercomputer, hosted by CINECA, and the computational resources provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS), funded by the Swedish Research Council. Additionally, S.S. and X.L. acknowledge the Swedish Research Council for financial support.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

- [1] U.S. DOE Nuclear Energy Research Advisory Committee and the Generation IV International Forum, A technology roadmap for Generation IV nuclear energy systems, Technical Report No. GIF-002-00 (U.S. DOE/Generation IV International Forum, 2002).
- [2] T. R. Allen and D. C. Crawford, Lead-cooled fast reactor systems and the fuels and materials challenges, *Sci. Technol. Nucl. Install.* **2007**, 097486 (2007).
- [3] International Atomic Energy Agency, Status of Fast Reactor Research and Technology Development, IAEA-TECDOC-1691, IAEA, Vienna (2013).
- [4] C. Petersson, P. Szakálos, and D. Dietrich Stein, Slow strain rate testing of Fe-10Cr-4Al ferritic steel in liquid lead and lead-bismuth eutectic, *Nucl. Mater. Energy* **34**, 101403 (2023).
- [5] F. Garner, Irradiation performance of cladding and structural steels in liquid metal reactors, *Materials Science and Technology* (John Wiley & Sons, New York, 2006).
- [6] F. Dehlin, J. Wallenius, and S. Bortot, An analytic approach to the design of passively safe lead-cooled reactors, *Ann. Nucl. Energy* **169**, 108971 (2022).
- [7] P. H. Gruber, J. Frostevar, and F. Akhtar, FeCrAl/15-15Ti composite tubes as LFR fuel cladding, *J. Nucl. Mater.* **631**, 156823 (2026).
- [8] P. Yvon, M. Le Flem, C. Cabet, and J. L. Seran, Structural materials for next generation nuclear systems: Challenges and the path forward, *Nucl. Eng. Des.* **294**, 161 (2015).
- [9] J. Ejenstam and P. Szakálos, Long term corrosion resistance of alumina forming austenitic stainless steels in liquid lead, *J. Nucl. Mater.* **461**, 164 (2015).
- [10] H. Liu, G.-H. Lei, and H.-F. Huang, Review on synergistic damage effect of irradiation and corrosion on reactor structural alloys, *Nucl. Sci. Tech.* **35**, 57 (2024).
- [11] P. Scott, A review of irradiation assisted stress corrosion cracking, *J. Nucl. Mater.* **211**, 101 (1994).
- [12] K. S. Mao, C. P. Massey, Y. Yamamoto, K. A. Unocic, M. N. Gussev, D. Zhang, S. A. Briggs, O. Karakoc, A. T. Nelson, K. G. Field, and P. D. Edmondson, Improved irradiation resistance of accident-tolerant high-strength FeCrAl alloys with heterogeneous structures, *Acta Mater.* **231**, 117843 (2022).
- [13] C. Liu, H. Ma, P. Fan, K. Li, Q. Zhang, A. Du, W. Feng, X. Su, S. Zhu, and D. Yuan, Cavity swelling of 15-15Ti steel at high doses by ion irradiation, *Materials* **17**, 925 (2024).
- [14] K. A. Terrani, N. A. Capps, M. J. Kerr, C. A. Back, A. T. Nelson, B. D. Wirth, S. L. Hayes, and C. R. Stanek, Accelerating nuclear fuel development and qualification: Modeling and simulation integrated with separate-effects testing, *J. Nucl. Mater.* **539**, 152267 (2020).
- [15] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* **50**, 17953 (1994).
- [16] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* **59**, 1758 (1999).
- [17] J. B. Piochaud, T. P. C. Klaver, G. Adjanor, P. Olsson, C. Domain, and C. S. Becquart, First-principles study of point defects in an fcc Fe-10Ni-20Cr model alloy, *Phys. Rev. B* **89**, 024101 (2014).
- [18] R. Hafner, D. Spisák, R. Lorenz, and J. Hafner, Does density-functional theory predict a spin-density-wave ground state for Cr? *J. Phys.: Condens. Matter* **13**, L239 (2001).
- [19] H. Amara, C. C. Fu, F. Soisson, and P. Maugis, Aluminum and vacancies in α -iron: Dissolution, diffusion, and clustering, *Phys. Rev. B* **81**, 174101 (2010).
- [20] H. Pitkänen, M. Alatalo, A. Puisto, M. Ropo, K. Kokko, M. P. J. Punkkinen, P. Olsson, B. Johansson, S. Hertzman, and L. Vitos, *Ab initio* study of the phase stability in paramagnetic duplex steel alloys, *Phys. Rev. B* **79**, 024108 (2009).
- [21] I. A. Abrikosov, A. E. Kissavos, F. Liot, B. Alling, S. I. Simak, O. Peil, and A. V. Ruban, Competition between magnetic structures in the Fe rich fcc FeNi alloys, *Phys. Rev. B* **76**, 014434 (2007).
- [22] D. Costa, G. Adjanor, C. Becquart, P. Olsson, and C. Domain, Vacancy migration energy dependence on local chemical environment in Fe-Cr alloys: A density functional theory study, *J. Nucl. Mater.* **452**, 425 (2014).
- [23] E. del Rio, J. M. Sampedro, H. Dogo, M. J. Caturla, M. Caro, A. Caro, and J. Manuel Perlado, Formation energy of vacancies in FeCr alloys: Dependence on Cr concentration, *J. Nucl. Mater.* **408**, 18 (2011).
- [24] J. Ejenstam, M. Thuvander, P. Olsson, F. Rave, and P. Szakalos, Microstructural stability of Fe-Cr-Al alloys at 450–550°C, *J. Nucl. Mater.* **457**, 291 (2015).
- [25] L. Delczeg, B. Johansson, and L. Vitos, *Ab initio* description of monovacancies in paramagnetic austenitic Fe-Cr-Ni alloys, *Phys. Rev. B* **85**, 174101 (2012).
- [26] T. P. C. Klaver, D. J. Hepburn, and G. J. Ackland, Defect and solute properties in dilute Fe-Cr-Ni austenitic alloys from first principles, *Phys. Rev. B* **85**, 174111 (2012).
- [27] J. Rogal, S. V. Divinski, M. W. Finnis, A. Glensk, J. Neugebauer, J. H. Perepezko, S. Schuwalow, M. H. F. Sluiter, and B. Sundman, Perspectives on point defect thermodynamics, *Physica Status Solidi (B)* **251**, 97 (2014).
- [28] T. Schuler, M. Nastar, K. Li, and C.-C. Fu, Towards accurate thermodynamics from random energy sampling, *Acta Mater.* **276**, 120074 (2024).
- [29] Y. Zhang, A. Manzoor, C. Jiang, D. Aidhy, and D. Schwen, A statistical approach for atomistic calculations of vacancy formation energy and chemical potentials in concentrated solid-solution alloys, *Comput. Mater. Sci.* **190**, 110308 (2021).
- [30] L. Vitos, H. L. Skriver, B. Johansson, and J. Kollár, Application of the exact muffin-tin orbitals theory: The spherical cell approximation, *Comput. Mater. Sci.* **18**, 24 (2000).
- [31] A. Zunger, S.-H. Wei, L. G. Ferreira, and J. E. Bernard, Special quasirandom structures, *Phys. Rev. Lett.* **65**, 353 (1990).
- [32] G. Kresse and J. Hafner, *Ab initio* molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium, *Phys. Rev. B* **49**, 14251 (1994).
- [33] G. Kresse and J. Furthmüller, Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* **6**, 15 (1996).
- [34] G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **54**, 11169 (1996).
- [35] B. L. Gyorffy, Coherent-potential approximation for a nonoverlapping-muffin-tin-potential model of random substitutional alloys, *Phys. Rev. B* **5**, 2382 (1972).

- [36] L. Vitos, I. A. Abrikosov, and B. Johansson, Anisotropic lattice distortions in random alloys from first-principles theory, *Phys. Rev. Lett.* **87**, 156401 (2001).
- [37] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [38] E. R. Davidson, in *Methods in Computational Molecular Physics*, edited by G. H. F. Dierksen and S. Wilson, NATO Advanced Study Institute, Series C, Vol. 113 (Plenum, New York, 1983), pp. 95–115.
- [39] B. Liu, in *Numerical Algorithms in Chemistry: Algebraic Methods*, edited by C. Moler and I. Shavitt (Lawrence Berkeley Laboratory, University of California, 1978), pp. 49–54.
- [40] J. S. Wróbel, M. R. Zemła, D. Nguyen-Manh, P. Olsson, L. Messina, C. Domain, T. Wejrzanowski, and S. L. Dudarev, Elastic dipole tensors and relaxation volumes of point defects in concentrated random magnetic Fe-Cr alloys, *Comput. Mater. Sci.* **194**, 110435 (2021).
- [41] D. Gehringer, M. Friák, and D. Holec, Models of configurationally-complex alloys made simple, *Comput. Phys. Commun.* **286**, 108664 (2023).
- [42] A. Stukowski, Visualization and analysis of atomistic simulation data with OVITO-the Open Visualization Tool, *Modell. Simul. Mater. Sci. Eng.* **18**, 015012 (2010).
- [43] L. Vitos, *Computational Quantum Mechanics for Materials Engineers: The EMTO Method and Applications* (Springer, Berlin, 2007).
- [44] B. L. Gyorffy, A. J. Pindor, J. Staunton, G. M. Stocks, and H. Winter, A first-principles theory of ferromagnetic phase transitions in metals, *J. Phys. F: Met. Phys.* **15**, 1337 (1985).
- [45] P. Olsson, I. Abrikosov, L. Vitos, and J. Wallenius, *Ab initio* formation energies of Fe-Cr alloys, *J. Nucl. Mater.* **321**, 84 (2003).
- [46] A. J. Pindor, J. Staunton, G. M. Stocks, and H. Winter, Disordered local moment state of magnetic transition metals: A self-consistent KKR CPA calculation, *J. Phys. F: Met. Phys.* **13**, 979 (1983).
- [47] A. Kissavos, S. Simak, P. Olsson, L. Vitos, and I. Abrikosov, Total energy calculations for systems with magnetic and chemical disorder, *Comput. Mater. Sci.* **35**, 1 (2006).
- [48] H. King, Quantitative size-factors for metallic solid solutions, *J. Mater. Sci.* **1**, 79 (1966).
- [49] P. Olsson, T. P. C. Klaver, and C. Domain, *Ab initio* study of solute transition-metal interactions with point defects in bcc Fe, *Phys. Rev. B* **81**, 054102 (2010).
- [50] D. Sheppard, P. Xiao, W. Chmielewski, D. D. Johnson, and G. Henkelman, A generalized solid-state nudged elastic band method, *J. Chem. Phys.* **136**, 074103 (2012).
- [51] G. Henkelman, B. P. Uberuaga, and H. Jónsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, *J. Chem. Phys.* **113**, 9901 (2000).
- [52] L. Messina, M. Nastar, N. Sandberg, and P. Olsson, Systematic electronic-structure investigation of substitutional impurity diffusion and flux coupling in bcc iron, *Phys. Rev. B* **93**, 184302 (2016).
- [53] R. Soulaïrol, C.-C. Fu, and C. Barreteau, Structure and magnetism of bulk Fe and Cr: From plane waves to lcao methods, *J. Phys.: Condens. Matter* **22**, 295502 (2010).
- [54] A. R. Warwick, J. B. J. Chapman, D. Nguyen-Manh, P.-W. Ma, and S. L. Dudarev, *Ab initio* relaxation volumes of transition metal solutes in iron and tungsten, *Phys. Rev. Mater.* **10**, 045402 (2026).
- [55] S. S. Shapiro and M. B. Wilk, An analysis of variance test for normality (complete samples), *Biometrika* **52**, 591 (1965).
- [56] P. Olsson, C. Domain, and J. Wallenius, *Ab initio* study of Cr interactions with point defects in bcc Fe, *Phys. Rev. B* **75**, 014110 (2007).
- [57] E. Mansouri and P. Olsson, First-principles predictions of structural and magnetic phase stability in irradiated α -Fe, *Mater. Res. Lett.* **12**, 477 (2024).
- [58] I. Miháliková, M. Friák, N. Koutná, D. Holec, and M. Šob, An *ab initio* study of vacancies in disordered magnetic systems: A case study of Fe-rich Fe-Al phases, *Materials* **12**, 1430 (2019).
- [59] J.-H. Ke and A. M. Jokisaari, Effects of aluminum and molybdenum on the phase stability of iron-chromium alloys: A first-principles study, *JOM* **75**, 3208 (2023).
- [60] A. Galler, C. Taranto, M. Wallerberger, M. Kaltak, G. Kresse, G. Sangiovanni, A. Toschi, and K. Held, Screened moments and absence of ferromagnetism in FeAl, *Phys. Rev. B* **92**, 205132 (2015).
- [61] I. R. Magalhães, L. V. G. Chaves, V. F. de Castro, P. A. L. Reis, A. L. Costa, M. A. F. Veloso, and C. Pereira, Comparative analysis of different FeCrAl alloys in pressurized water reactors, *Nucl. Eng. Des.* **422**, 113109 (2024).
- [62] A. Vasilyev, S. Sokolov, N. Kolbasnikov, and D. Sokolov, Effect of alloying on the self-diffusion activation energy in γ -iron, *Phys. Solid State* **53**, 2194 (2011).
- [63] S.-L. Shang, B.-C. Zhou, W. Y. Wang, A. J. Ross, X. L. Liu, Y.-J. Hu, H.-Z. Fang, Y. Wang, and Z.-K. Liu, A comprehensive first-principles study of pure elements: Vacancy formation and migration energies and self-diffusion coefficients, *Acta Mater.* **109**, 128 (2016).
- [64] J. Kučera, B. Million, J. Růžicková, V. Foldyna, and A. Jakobová, Self-diffusion of iron in alpha-phase of iron and Fe-Cr alloys, *Acta Metall.* **22**, 135 (1974).
- [65] L. Mansur, Correlation of neutron and heavy-ion damage: II. the predicted temperature shift if swelling with changes in radiation dose rate, *J. Nucl. Mater.* **78**, 156 (1978).