

Impact of thermal excitations on the stabilization of the disordered VCoNi alloy

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The VCoNi alloy is a face-centered cubic medium-entropy alloy with exceptionally high yield strength, serving as a prototypical system for investigating short-range order and phase stability in compositionally complex alloys. However, density functional theory calculations underestimate the stability of the random solid solution by several hundred Kelvin. To resolve this discrepancy, we present accurate Gibbs energy calculations for both the random solid solution and a prototypical L_{12} ordered phase. Our findings reveal that vibrational and electronic excitations account for nearly half of the entropy difference between the ordered phase and disordered solid solution. These factors reduce the energy difference between the two phases by about one-third and help stabilize the solid solution. Our thermodynamic analysis is validated through direct comparison with experimental thermodynamic data.

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I. INTRODUCTION

There is considerable interest in quantifying and understanding the impact of short-range order (SRO) on the properties of compositionally complex alloys. For this purpose, the equimolar face-centered cubic (fcc) VCoNi alloy [1–10] has become a prototypical alloy system for studying SRO and its impact on materials' properties.

The VCoNi alloy forms a single-phase fcc solid solution when annealed at temperatures above 1173 K. Annealing at lower temperatures results in phase decomposition into σ and κ phases, along with transient L_{12} and SRO phenomena that depend on the annealing time [1,2,7]. Alloying with aluminum or titanium further stabilizes nanoscale L_{12} domains [8], while the introduction of Fe promotes hierarchical κ and L_{12} ordering [9].

In contrast to the experimentally reported stability, theoretical predictions based on density-functional theory (DFT) consistently underestimate the stability of the equiatomic

VCoNi fcc disordered solid solution [11,12]. For instance, Kostichenko *et al.* [11], employing a combination of ground-state DFT calculations, machine-learning potentials, and Monte Carlo simulations, predicted stability only down to approximately 1500 K, below which a long-range ordered L_{12} phase becomes thermodynamically favorable. Similarly, recent predictions by Cao *et al.* [12] suggest that this L_{12} ordering remains stable even at temperatures higher than 1500 K.

A critical factor influencing phase stability predictions is the inclusion of thermal lattice vibrations. It is well known that vibrational entropy differences between competing phases can significantly alter their relative thermodynamic stability [13,14]. For example, experimental studies have demonstrated that disordered CoV and NiV phases possess higher vibrational entropies compared to their ordered counterparts (L_{12} Co₃V and D022 Ni₃V) [15,16]. Despite recent efforts to incorporate vibrational entropy through approximate methods like the Debye model [12], a thorough investigation of the vibrational contributions in both the disordered and ordered phases of the VCoNi alloy is still needed. Such an analysis would be useful for accurately evaluating the stability of the disordered solid solution and for selecting the appropriate simulation techniques and theoretical framework for these types of alloys.

In the present work, we address this simulation gap by accurately calculating the vibrational Gibbs energies of the disordered and L_{12} -ordered phases of the VCoNi alloy. We employ machine-learning interatomic potentials combined with the direct upsampling approach [17], which results in full DFT-accuracy [17,18]. Our calculations explicitly account for electronic excitations and anharmonic vibrational effects,

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enabling a reliable assessment of their influence on ordering energies. Furthermore, we validate our theoretical predictions with experimental measurements of the thermal expansion coefficient and bulk modulus as a function of temperature. Our findings demonstrate that thermal lattice vibrations play a crucial role in stabilizing the disordered phase.

II. METHOD, COMPUTATIONAL, AND EXPERIMENTAL DETAILS

A. Finite-temperature calculations

We employ the direct upsampling approach [17], which utilizes machine learning interatomic potentials in combination with free energy perturbation to reach DFT accuracy in the Gibbs energy. The Gibbs energy $G(T, p)$ is computed as a function of temperature T , and at ambient pressure p , for both phases. It is obtained from the Helmholtz free energy $F(V, T)$ via the standard Legendre transformation $G(T, p) = F(V, T) + pV$, where V is the volume. The free energy is computed as:

$$F(V, T) = E_{0K}^{\text{DFT}}(V) + F_{\text{vib}}^{\text{MLIP}}(V, T) + \Delta F_{\text{vib+el}}^{\text{DFT}}(V, T) - TS_{\text{conf}}^{\text{ideal}}(T). \quad (1)$$

Here, E_{0K}^{DFT} denotes the static energy-volume curve calculated at 0 K and $F_{\text{vib}}^{\text{MLIP}}$ is the vibrational contribution including anharmonicity using thermodynamic integration and based on a machine-learning interatomic potential (MLIP). Further, $\Delta F_{\text{vib+el}}^{\text{DFT}}$ is the perturbative DFT correction to $F_{\text{vib}}^{\text{MLIP}}$ based on explicit DFT calculations (direct upsampling approach [17]). The final term, $S_{\text{conf}}^{\text{ideal}}$, represents the configurational entropy. Since the focus of the present work is on vibrational and electronic free-energy contributions, we approximate the configurational entropy by the ideal mixing expression, thereby neglecting short-range order effects. The perturbative correction $\Delta F_{\text{vib+el}}^{\text{DFT}}$ accounts for both the DFT correction to the MLIP energies evaluated on the vibrational configurations and the electronic free-energy contribution evaluated consistently on these configurations. We will discuss further below that the alloy is only weakly magnetic and therefore, we ignore explicit finite-temperature magnetic free energy contributions. We note, however, that all above mentioned contributions are calculated based on spin-polarized calculations, thus taking ground-state magnetic effects into account.

Detailed descriptions of the direct upsampling method, computational procedures for each free-energy contribution, and the extraction of thermodynamic properties from $F(V, T)$ are provided in Ref. [17]. The scripts are available as part of the direct upsampling package [19]. Briefly, our approach involves three main steps: (i) training an MLIP, here a moment tensor potential (MTP) [20,21], (ii) thermodynamic integration from a quasiharmonic reference to the MTP potential, and (iii) free-energy perturbation-based upsampling from MTP to DFT accuracy.

Finite-temperature molecular dynamics (MD) simulations during the thermodynamic integration step were carried out using Atomic Simulation Environment [22,23]. Subsequent DFT calculations for free-energy upsampling were performed as given in Sec. II B. The quasiharmonic reference potential

used as a reference for the thermodynamic integration was fitted at 20 K from snapshots generated with the MTP potential.

To more accurately separate quasiharmonic contributions, we also conducted DFT calculations using PHONOPY [24,25] with the finite displacement method. We employed a displacement amplitude of 0.03 Å and carried out calculations at four different volumes for a range of 11–12 Å³/atom. All other computational settings were chosen consistently with those used in the upsampling approach described in Sec. II B. While the k -point sampling used is adequate for accurate total energy calculations, it may not fully converge the forces. Nevertheless, it should provide a reliable qualitative separation of the quasiharmonic contributions, and it does not affect the final free energies in any way.

B. Density-functional theory calculations

Spin-polarized DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) 5.4.4 [26–28] in combination with the projector augmented wave (PAW) method [29]. Standard VASP PAW potentials (without semi-core p states) were used for V, Co, and Ni. Most of the calculations were performed using the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE) [30]. Tests treating s and p electrons for V explicitly as valence show robust phase energy differences of approximately 2%, a similar bulk modulus, and a slightly increased volume for both phases of about 0.7%. Some calculations were performed within the local density approximation (LDA) [31] to evaluate the impact of the approximation for the exchange-correlation (xc) functional, which will be discussed further below. The local magnetic moments were initialized ferromagnetically for Co and Ni, and antiparallel for V. We also evaluated other initializations, such as starting with all moments in a ferromagnetic configuration, but found that this only led to longer convergence cycles without achieving a lower energy state.

Initially, three cubic supercells containing 108 atoms each were generated for both the random solid-solution and the L1₂-ordered states to calculate ground-state energy-volume curves. Special quasi-random structures were utilized for the random solid solution, while structures with disorder on the M-site in L1₂-type ordered states were created. In both cases, the configurations were generated using the ICET package [32].

For the considered $3 \times 3 \times 3$ (108 atoms) supercells, a plane-wave basis set with an energy cutoff of 400 eV and a Monkhorst-Pack $4 \times 4 \times 4$ k -mesh were used for the self-consistent calculations. Ionic relaxations were performed for the atomic positions while keeping the cell shape fixed. The stopping criteria for the self-consistent electronic minimization and ionic relaxation were set to 10^{-4} and 10^{-3} eV per supercell.

The Methfessel-Paxton order 1 scheme was used with a smearing parameter of 0.1 eV. For the direct upsampling approach, the Fermi smearing method, with a smearing parameter corresponding to the evaluated temperatures, was used. To separate the electronic free energy contributions for further analysis, the electronic free energies were computed using their respective density of states.

C. Thermodynamic integration and upsampling

Based on the computed equations of state, we initially utilized a Debye model to estimate the relevant volume range for the free energy calculations, selecting volumes from 11 to 12.33 Å³/atom. We chose nine evenly spaced volumes within this range for DFT MD simulations. These simulations employed “low” DFT parameters, including a 250 eV cutoff, a single k -point, and an energy convergence criterion of 10⁻² eV per cell. A Langevin thermostat was set to 1500 K, and the MD simulation ran for 1500 steps with a timestep of 5 fs. We extracted every tenth configuration to fit level-8 moment tensor potentials (MTPs) [20,21], which were used to generate the physically relevant snapshots for training the more accurate high-level MTPs (level 20).

The low-level MTPs were then used in MD runs at 1300 K with 1 fs timesteps, generating 250 snapshots per volume. A total of 2500 snapshots were recalculated using accurate DFT settings (400 eV cutoff and $4 \times 4 \times 4$ k -points per 108-atom supercells), which were then used to fit the high-level MTPs, balancing accuracy and stability for subsequent thermodynamic integration. Further refinement of the high-level MTPs was carried out using five independent MD runs for each volume at 1300 K, each consisting of 100 000 steps with a time step of 1 fs using LAMMPS [33]. Configurations with extrapolation grade greater than 1 were extracted, and the simulations were stopped whenever a configuration with a grade above 2.5 was encountered. The selected configurations were then iteratively added to the training set using the select-add procedure [21] to avoid redundant structures. The potentials were retrained after each iteration, and this cycle was repeated until all five MD runs at each volume ran stably for 100 000 steps.

For the thermodynamic integration (TI), we constructed an effective quasiharmonic potential using the HIPHIVE package [34] based on MD snapshots at 20 K. To stabilize the TI, we performed 10 additional DFT calculations on configurations with minimal atomic distances, extracted from an MD using the effective quasiharmonic potential. This approach enhanced the stability of the TI, as outlined in Ref. [17].

The thermodynamic integration was performed over 4500 configurations sampled from MD runs with a timestep of 0.5 fs and an interval of 100 fs (where the first 1000 fs were disregarded for equilibration), using 20 λ values evenly spaced between 0 and 1. We sampled 9 temperatures ranging from 185 K to 1300 K at each volume. To achieve DFT-level accuracy, including electronic free energies, free energy perturbation calculations were conducted with 70 DFT calculations for each volume-temperature point, incorporating Fermi smearing as discussed above to account for electronic excitations. For the selected number of snapshots, statistical errors are below 0.6 meV/atom at all considered temperature-volume points.

D. Experimental details

A VCoNi single crystal was produced using the Bridgman technique and homogenized at 1473 K for 24 h. After homogenization, the single crystal was found to be chemically homogeneous at the mm and μ m-length scales. A cuboid with edge lengths of $5 \times 6 \times 7$ mm³ was prepared by electric

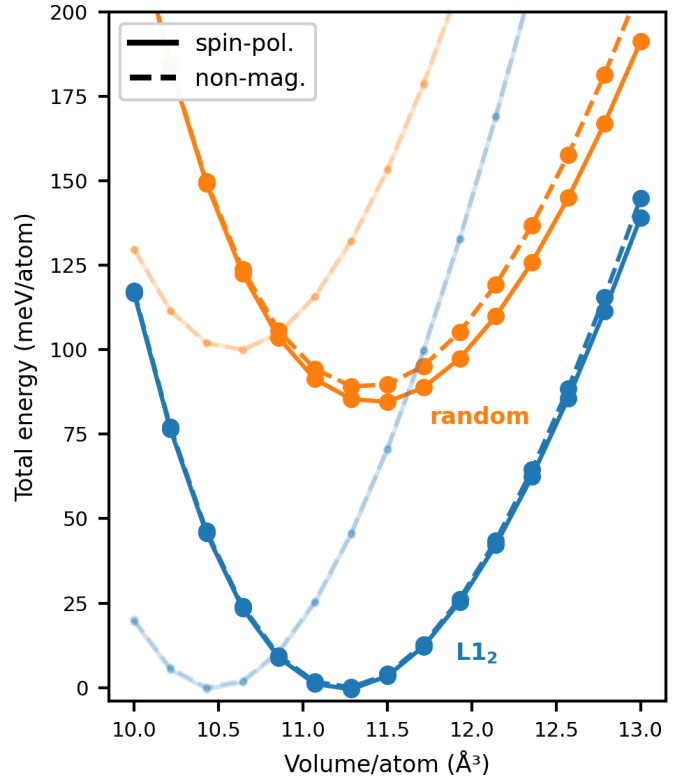


FIG. 1. Energy-volume curves for the L1₂-ordered phase (in blue) and random solid solution (in orange) of fcc VCoNi calculated using LDA (smaller symbols and lighter colors) and PBE functionals (larger symbols, stronger colors), with spin- (solid lines) and nonspin polarized calculations (dashed lines). The most pronounced changes between LDA and PBE results are the different equilibrium volumes and the weaker impact of magnetism within LDA.

discharge machining, ensuring that its faces were parallel to {100} crystallographic planes. Its thermal dilatation behavior between 100 K and 673 K was subsequently investigated using a Netzsch DIL402C dilatometer, with a heating/cooling rate of 2 K/min in a helium purge gas atmosphere. A lattice parameter of 3.60 Å at 293 K has been reported for the random alloy [1,7]. This value was corrected to 0 K using the experimental thermal strain in combination with a corresponding Einstein model for extrapolation to temperatures below 100 K. The elastic properties were studied in the temperature range 100 K–673 K employing resonant ultrasound spectroscopy. The experimental bulk modulus at 100 K is 188 GPa, providing a lower bound, and a linear extrapolation to 0 K yields an upper bound of 192 GPa. We therefore adopt an uncertainty of ± 2 GPa around the mean value of 190 GPa.

III. RESULTS AND DISCUSSION

A. Groundstate energies: Impact of xc-functional, SQS realization, and ground-state magnetism

Figure 1 displays the energy-volume curves computed using both the LDA and the PBE functionals. Each curve corresponds to an average of the ground-state energies obtained from three different SQS and three L1₂ realizations to visualize the trends more clearly. The corresponding averaged

TABLE I. Comparison of the equation-of-state properties at 0 K, bulk modulus B_{eq} , its pressure derivative B'_{eq} , equilibrium volume V_{eq} , and the 0 K energy difference ΔE between the $L1_2$ -ordered phase and the disordered fcc solid solution in VCoNi, using LDA and PBE functionals with spin-polarization. The standard deviation among the three theoretical configurations chosen for each scenario is given in parentheses, except for the experimental B_{eq} , where the number in parentheses represents the estimated extrapolation uncertainty (see Sec. II D for details).

System	B_{eq} (GPa)	B'_{eq}	V_{eq} ($\text{\AA}^3/\text{atom}$)	ΔE (meV/atom)
LDA $L1_2$	273(1)	4.7(1)	10.480(3)	99(2)
LDA random alloy	259(1)	4.8(2)	10.592(4)	0
PBE $L1_2$	218(1)	5.1(1)	11.239(3)	84(2)
PBE random alloy	204(2)	4.8(1)	11.418(8)	0
Experiment random alloy	190(2)		11.60	

equilibrium bulk moduli B_{eq} , their pressure derivatives B'_{eq} , and atomic volumes V_{eq} , at $T = 0$ K, which were derived from fits using the Vinet equation of state, are presented in Table I, along with the standard deviations among the three structural realizations (indicated in parentheses). The small variation in these values suggests that the selected supercell size is sufficiently large to effectively capture the effects of configurational randomness in the supercell realizations.

The differences in the 0 K energy-volume curves obtained using the PBE and LDA functionals, as shown in Fig. 1, are most pronounced in the values for the equilibrium volumes V_{eq} . As anticipated, LDA yields systematically smaller V_{eq} values than PBE, reflecting its known tendency to overbind. Also, the bulk moduli are much stiffer as compared to the PBE counterparts, see Table I. Figure 2 illustrates the corresponding energy differences as a function of volume. Notably, at smaller volumes, the energy differences between the two structural configurations are remarkably similar across both functionals, but start to deviate systematically in the experimentally relevant regime.

Spin polarization was found to be negligible in the LDA calculations, likely due to the lower equilibrium volumes, reflecting the tendency of magnetic moments in transition

metals to decrease under compression. However, for PBE, the random alloy exhibits a slight energetic stabilization due to magnetism. This magnetic contribution, although weak, is consistently observed mostly within the PBE framework. Given that the experimental lattice constants are also closer to the PBE results (Table I), all subsequent calculations were carried out using spin-polarization and the PBE functional.

The energy differences shown in Fig. 2 emphasize the significant effect that volume expansion has on the relative energetic stability of the two configurations, highlighting the importance of implicit lattice vibrational effects. Notably, the equilibrium volume derived from zero-temperature PBE calculations is lower than the extrapolated experimental value at 0 K. Considering that the experimentally observed ordering temperature is around 1200 K, the effect due to thermal expansion and explicit vibrational entropy is likely even more pronounced. The fact that the LDA results strongly underestimates the experimental lattice constant further corroborates the choice of proceeding with the PBE calculations.

B. Thermal properties of the disordered solid solution

Figure 3 summarizes the temperature-dependent properties of the disordered VCoNi solid solution. The experimental data for the relative linear expansion and its coefficient, shown in Figs. 3(a) and 3(b), respectively, are in excellent agreement with the theoretical predictions. There is a weak impact of explicit anharmonic contributions, whereas electronic free energies appear rather volume independent and do not contribute to the expansion. The calculated bulk modulus, shown in Fig. 3(c), accurately reproduces the experimental data, though its magnitude at a given temperature is about 5% higher. A similar good agreement is obtained for the temperature dependence of the independent elastic stiffness coefficients (c_{ij}), which we discuss elsewhere. The good agreement between the computational predictions and experimental values indicates that the temperature-dependent vibrational and electronic contributions are well captured. The configurational entropy, treated within the ideal mixing approximation, is volume independent [Eq. (1)] and therefore does not affect the thermodynamic properties shown in Figs. 3(a)–3(d); for reference, it is included in Fig. 3(f).

The heat capacity curves in Fig. 3(d) illustrate that there are nonvanishing electronic contributions. These contributions are also pronounced in the Gibbs energies, Fig. 3(e), which are referenced to the quasiharmonic results for better visualization. The same holds for the entropy shown in Fig. 3(f),

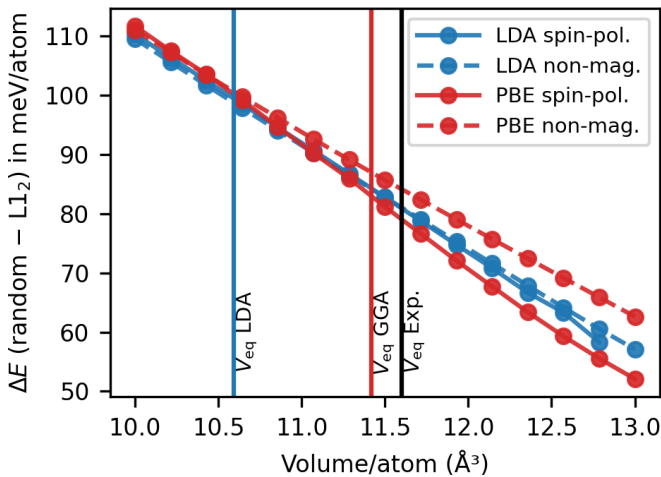


FIG. 2. Energy differences between $L1_2$ -ordered and random configurations computed with LDA (blue) and PBE (red) are shown with and without spin polarization (see solid and dashed lines, respectively). The theoretical equilibrium and extrapolated experimental volume at $T = 0$ K for the random alloy are shown as solid vertical lines.

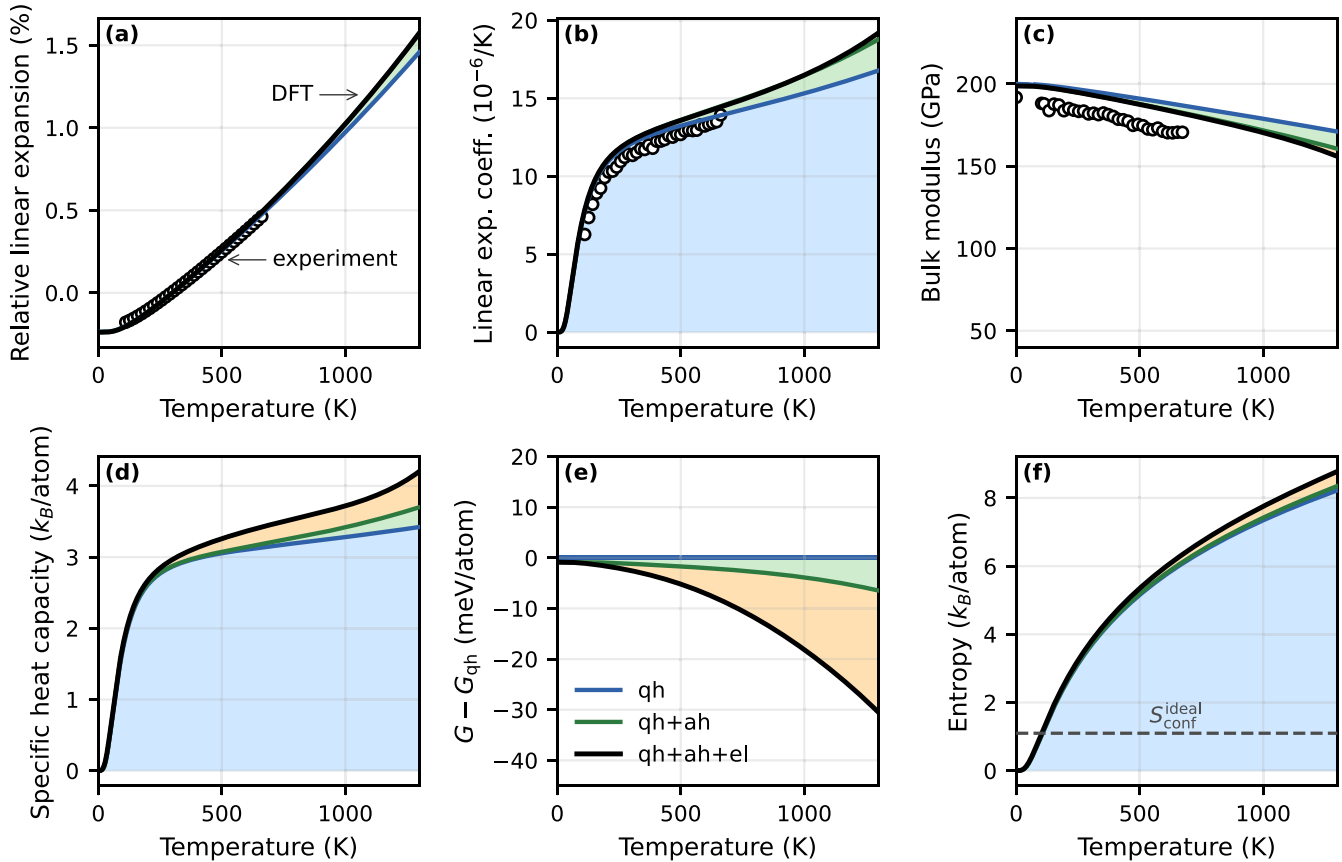


FIG. 3. The temperature dependence of the random VCoNi alloy is presented for: (a) relative linear expansion (referenced to room temperature), (b) linear expansion coefficient, (c) bulk modulus, (d) heat capacity, (e) the difference in Gibbs energy compared to the quasiharmonic energy, and (f) entropy. The results for the quasiharmonic (qh) Gibbs energies are illustrated with solid blue lines, while the Gibbs energies that additionally account for explicit anharmonic effects (qh+ah) and electronic free energies (qh+ah+el) are displayed in solid green and solid black lines, respectively. In panel (f), the dashed horizontal line indicates the ideal configurational entropy.

which likewise highlights the large contribution of the quasiharmonic entropy.

When comparing the quasiharmonic results with the explicit anharmonic and electronic free energy contributions, the quasiharmonic results dominate the thermodynamic contributions in this temperature range. In contrast, the electronic and anharmonic effects are relatively minor. However, when evaluating the differences between competing phases, these smaller terms do not necessarily cancel out and can influence the relative stability. We will address this point in the following section.

C. Impact of thermal excitations on ordering energies

The Gibbs energy differences between the disordered fcc solid solution and the $L1_2$ -ordered phase, i.e., without the static energy difference at 0 K, are shown in Fig. 4(a). Figure 4 includes vibrational (harmonic, quasiharmonic, and explicit anharmonic) and electronic contributions. The configurational entropy, treated within the ideal mixing approximation, is intentionally omitted to isolate the other effects. All these other thermal contributions to the Gibbs energy difference between the disordered and ordered phases are negative, indicating that each one leads to a net stabilization of the solid solution. The quasiharmonic term provides the largest negative contri-

bution, followed in magnitude by the anharmonic correction and then the electronic free-energy term. In the quasiharmonic term, the harmonic component represented by a dashed line is dominant, while thermal expansion adds a minor correction. When these differences are compared to the individual Gibbs energies of the disordered solid solution, Fig. 3(e), it is evident that the electronic corrections tend to cancel more effectively than the anharmonic ones. Overall, the vibrational and electronic thermal excitations reduce the ordering energy by roughly one third relative to the 0 K static energy difference of 84 meV per atom (Table I). This reduction is consistent with the overestimation of the transition temperature reported in Ref. [11] when thermal excitations are neglected.

The differences in entropy between the disordered and ordered phases, shown in Fig. 4(b), are all positive. This indicates that the disordered solid solution gains more entropy from each thermal contribution at finite temperatures compared to its ordered counterpart. Similar to the Gibbs energies, the quasiharmonic contribution is the most significant, with its harmonic part dominating, followed by anharmonic and electronic terms. The explicit electronic entropy term is comparatively small. In the present alloy, it contributes roughly 10% of the total thermal correction, consistent with the trends reported in Ref. [11]. To also put these entropy terms into perspective, we estimated the ideal chemical mixing entropy

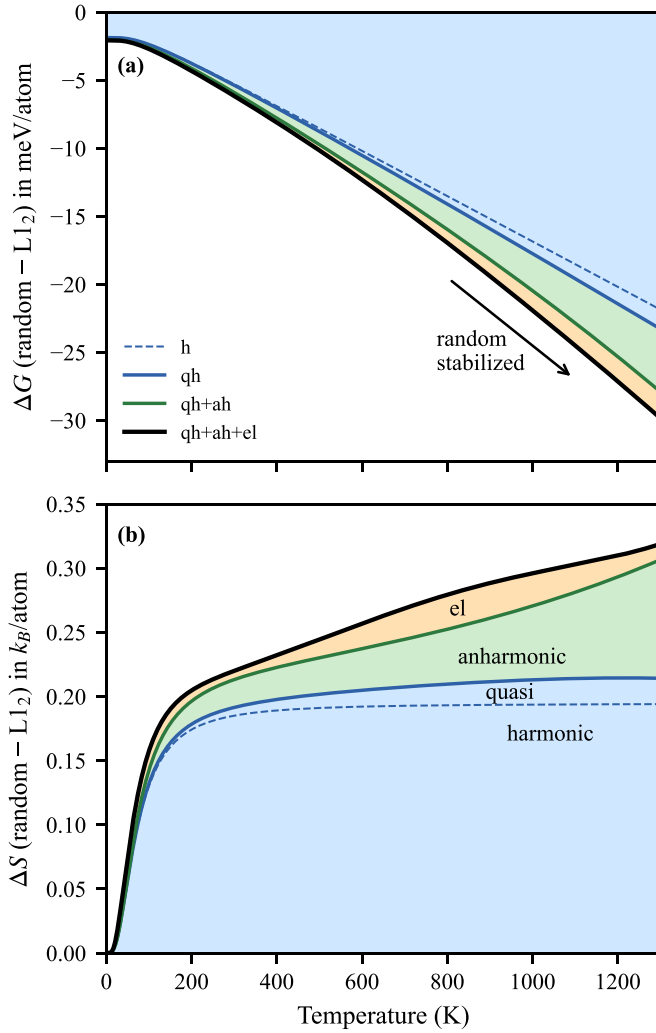


FIG. 4. Temperature dependence of the differences between the disordered random phase and the L_{12} -ordered phase. (a) Gibbs free-energy differences due to vibrations and electronic excitations (excluding the static $T = 0$ K contribution). (b) Entropy differences due to vibrations and electronic contributions. Quasiharmonic results (qh) are shown in blue, quasiharmonic plus explicit anharmonic contributions ($qh+ah$) in green, and quasiharmonic plus electronic free-energy contributions ($qh+ah+el$) in black.

in the L_{12} phase. For this purpose, we assumed that V occupies the corner sites, and that Co, Ni, and the remaining V atoms mix ideally on the other sites. This results in an idealized entropy difference of $0.375 k_B$ per atom between the disordered solid solution and the L_{12} phase. At the highest temperature considered, 1300 K, we break down the total entropy difference into vibrational (harmonic, quasiharmonic, and anharmonic) and electronic contributions (as shown in Fig. 5), with the ideal mixing term provided for reference. The lower dashed line in the qh bar represents the harmonic component, which contributes the most to the vibrations, while the remaining part indicates the contribution from thermal expansion. The pie chart demonstrates that thermal excitations account for nearly half of the entropy differences between the disordered solid solution and the ordered- L_{12} phase at the relevant temperatures. Among these contributions, quasi-

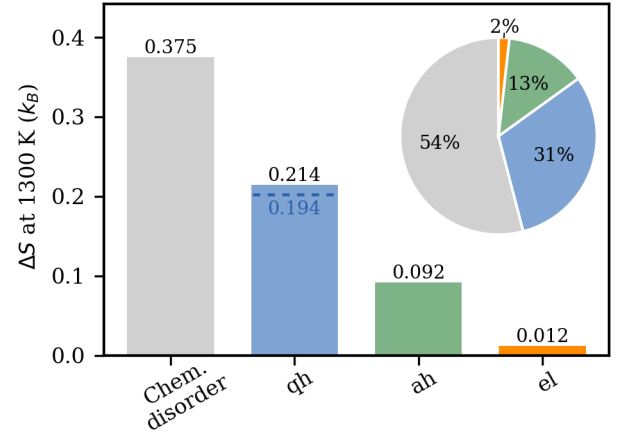


FIG. 5. The combined bar and inset pie chart shows the entropy differences between the disordered and ordered- L_{12} phases at 1300 K separated into individual contributions: ideal chemical disorder mixing, quasiharmonic and explicit anharmonic vibrational terms, as well as electronic contributions. The bar chart displays the absolute contributions in units of k_B , while the inset pie chart illustrates their relative fractions. The dashed line in the bar for the quasiharmonic result indicates its harmonic contribution.

harmonic vibrational entropy dominates, accounting for the majority of the effect, while the combined contributions from anharmonic and electronic effects add 15% to the total entropy gain and can clearly not be neglected when considering the phase stability.

D. Constant pressure versus constant volume

Many perturbative treatments of capturing the chemical interactions are performed at fixed volume [11,35] as they aim to mimic, e.g., SRO at high temperatures. A fixed-volume assumption could, however, limit an accurate transition temperature estimation if the competing phases reveal different equilibrium volumes, as in the present case. To isolate the role of this constraint, Fig. 6 compares two scenarios: (i) a constant-pressure case, where each phase is evaluated at its T -dependent zero-pressure volume (black solid line), and (ii) a constant-volume case, constrained to the equilibrium volume of the random solid solution (orange line) or the equilibrium volume of L_{12} phase (blue line). Imposing fixed volumes decreases the total energy difference by about 13 meV/atom, which is small compared to the Gibbs free energy correction of approximately 33 meV. The black dashed line highlights the total energy contribution under fixed pressure, which changes only slightly with temperature. Comparing the volume and pressure-constrained scenarios, it turns out that a fixed volume approximation accounts for only part of the stabilization. The energy correction due to explicit thermal excitations at constant pressure is about twice as large.

These results also show that fixed-volume calculations, although lacking explicit vibrational excitations, can reproduce part of the stabilization of the disordered phase. In VCoNi, the disordered solid solution has a larger equilibrium volume and a softer equation of state than the ordered- L_{12} phase. Imposing a constrained volume therefore lowers the relative energy of the disordered phase, partially mimicking

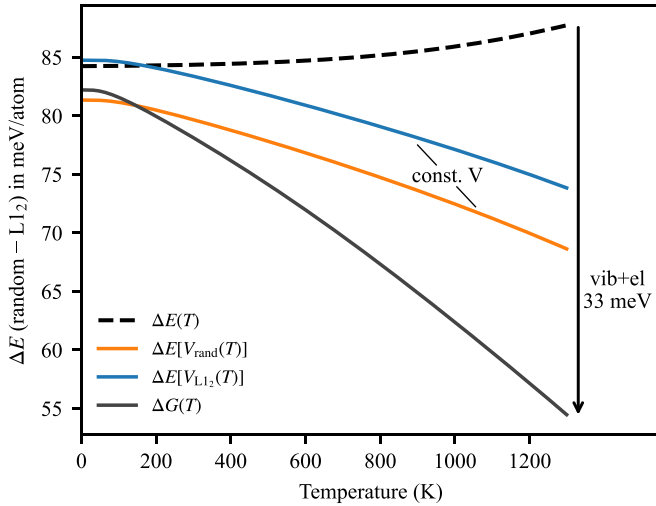


FIG. 6. Energy differences between the disordered solid solution and the L_{12} phase are presented. The total energy differences are shown in black along the temperature-dependent volumes at zero pressure. Additionally, the total energy differences are illustrated along the fixed equilibrium volumes of both the disordered solid solution and the L_{12} phase. For comparison, the total Gibbs energy difference at constant pressure, which includes all terms as in Fig. 4, is also displayed.

the effect of lattice vibrations, which preferentially stabilize higher-energy phases. In the current system, this fixed-volume compensation captures approximately one-third of the full vibrational (and electronic) stabilization. The magnitude of this effect is system-dependent and becomes smaller when competing phases exhibit similar equilibrium volumes or curvatures. While configurational entropy constitutes the most significant entropic contribution to the stability of the random alloy, explicit vibrational free energies remain the dominant thermal correction beyond configurational entropy itself. A fixed-volume method can serve, however, as a practical first-order correction due to its lower computational cost.

IV. SUMMARY AND CONCLUSION

We examined two configurations for VCoNi—a disordered fcc solid solution and an M_3V -ordered L_{12} structure on the fcc lattice—using both LDA and PBE exchange correlation functionals to assess ground-state energetics. We also evaluated thermodynamic properties from harmonic phonons to fully anharmonic free-energy corrections, including electronic excitations.

The energy-volume curves show that LDA systematically underestimates equilibrium volumes compared to PBE, yet both functionals yield similar energy differences between disordered and ordered phases at fixed volumes. Spin polarization is negligible in LDA (due to the smaller volumes) but slightly stabilizes the disordered solid solution in PBE. Both functionals underpredict the experimental lattice parameter and overestimate the bulk modulus, though PBE agrees more closely with the experiment.

State-of-the-art machine-learning-based molecular dynamics simulations using thermodynamic integration and free energy perturbation techniques yield anharmonic and elec-

tronic free-energy corrections that, while smaller than the quasiharmonic term, sum to roughly 25% of the ideal-mixing entropy. Together with the quasiharmonic contributions, this results in thermal excitations accounting for about half of the total entropy difference between the ordered and disordered phases. The thermodynamic quantities of the disordered solid solution are in good agreement with the experimental data, supporting the reliability of the computational approach.

Many simulations are based on a fixed-volume assumption, which tends to be reliable for short-range order. However, this assumption can be misleading when competing phases have different equilibrium volumes. Our comparison indicates that while raising the fixed volume can somewhat reduce the energy differences, it only accounts for about one-third of the stabilization achieved through full thermal excitations. The inclusion of the set of relevant thermal excitations, as achieved here for fully anharmonic vibrations and electronic excitations, is thus critical for a correct prediction of phase stabilities.

Beyond the ideal-mixing approximation, a natural next step is to explicitly examine the coupling between chemical short-range order and thermal excitations. Short-range order can alter vibrational and electronic free energies, while thermal excitations may, in turn, influence ordering tendencies and transition temperatures. A comprehensive approach that fully couples configurational, vibrational, and electronic degrees of freedom, therefore, represents a promising direction.

To even further improve accuracy, one could consider longitudinal spin fluctuations, which may have an impact on the chemical interactions in this alloy [11]. Whether such fluctuations also couple to lattice dynamics and to what extent these effects may cancel out when comparing the competition between phases will, however, require more advanced techniques (such as, e.g., spin-lattice simulations [36]). Moreover, residual volume and bulk modulus discrepancies at 0 K hint that more advanced functionals could further improve the predictions.

Overall, our results reveal that, in multicomponent alloys consisting of elements with significant size and mass differences, such as VCoNi alloys, vibrational entropy can decisively impact the phase stability and, in the present case, significantly contribute to the stabilization of the random solution and shift phase-transition behavior. This finding is especially relevant given recent advancements in alloying VCoNi-based alloys towards stabilization of L_{12} precursors for improved mechanical properties [8,10]. Furthermore, our results provide a crucial benchmark dataset for fitting and fine-tuning universal interatomic potentials, which could be used to pre-screen candidate structures or even replace some of the explicit DFT calculations.

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to manuscript review and editing. B.G. contributed to formal analysis, manuscript review, and editing.

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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.

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