Solubility of Boron, Carbon, and Nitrogen in Transition Metals: Getting Insight into Trends from First-Principles Calculations

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*Supporting Information

ABSTRACT: Efficient chemical vapor deposition synthesis of two-dimensional (2D) materials such as graphene, boron nitride, and mixed BCN systems with tunable band gaps requires precise knowledge of the solubility and mobility of B/C/N atoms in the transition metals (TMs) used as substrates for the growth. Yet, surprisingly little is known about these quantities either from experiments or simulations. Using first-principles calculations, we systematically study the behavior of B/C/N impurity atoms in a wide range of TMs. We compute formation energies of B/C/N interstitials and demonstrate that they exhibit a peculiar but common behavior for TMs in different rows of the periodic table, as experimentally observed for C. Our simulations indicate that this behavior originates from an interplay between the unit cell volume and filling of the d-shell electronic states of the metals. We further assess the vibrational and electronic entropic contributions to the solubility, as well as the role of anharmonic effects. Finally, we calculate the migration barriers, an important parameter in the growth kinetics. Our results not only unravel the fundamental behavior of interstitials in TMs but also provide a large body of reference data, which can be used for optimizing the growth of 2D BCN materials.

Graphene and single sheets of hexagonal boron nitride are novel two-dimensional (2D) materials with a similar atomic structure but drastically different electronic properties: while the former is a semimetal with zero bandgap, the latter is a wide gap insulator. Both materials can be grown by chemical vapor deposition (CVD) methods on various transition metal (TM) and alloy substrates. As graphene-BN lateral and vertical heterostructures and hybrid BCN systems have been predicted to exhibit unique electronic and optical properties, several attempts to synthesize such systems have been made. However, precise control over the atomic structure of the mixed material has not yet been achieved, which may be related to the choice of the substrate metal used and nonoptimal growth parameters. In the context of the CVD growth of BCN systems, one of the key issues is the solubility and diffusivity of B/C/N atoms in the metal. When solubility is high (as e.g., C in Ni), the metal can take up a considerable amount of the species, and growth can proceed via supersaturation and segregation. The species dissolved in the metal can give rise to precipitation of undesirable extra layers of the material upon cooling the system. Even for metals with low solubility (e.g., Au or Cu), the behavior of interstitials in the bulk is important in the context of ion-irradiation-mediated growth of graphene and potentially other 2D materials: successive implantation of different atoms in the metal substrate well above the solubility limit followed by annealing of the sample can give rise to nucleation of new 2D mixed systems on metal surfaces.

At the same time, relatively little is known about the solubility and mobility of B/C/N atoms in TMs. Apart from the vast literature on the solubility of C in Fe, the experimental data for other metals is rather scarce, and the reported experimental results frequently contradict each other. For example, solubility of C in Au was found to be lower than that in Rh, Ru, and Re, whereas the opposite was reported later. Likewise, based on the old data on interstitial formation energies, the solubility of C in Cu and Ni should be roughly the same, which is clearly at odds with numerous experimental observations of graphene growth on these metals, and with the results of first-principles calculations. Furthermore, the reported values of solubility of C in Cu at 1000°C differ by about 3 orders of magnitude, and they may be compromised by the presence of grain boundaries, by sample preparation methods used, and even by film thickness and associated
The climbing-image nudged-elastic-band method was zone sampled with supercells composed of atoms. The bulk metals were also studied using the XC functional. The bulk metals were calculated in supercells using a k-point mesh. The vibrational free energy was calculated for FCC and HCP metals. The results of simulations were also necessary displacement and force constant matrices. The force constant matrix was then diagonalized directly in real space to obtain the vibrational frequencies of the supercell, rather than employing the common procedure of Fourier transforming the force constant matrix to obtain the dynamical matrix, which is then diagonalized and interpolated in reciprocal space. This is crucial to obtain a consistent convergence behavior as a function of supercell size. Supporting Information Figure S2 demonstrates the agreement between our implementation and the one used by Glensk et al.

As impurity atoms are known to occupy interstitials positions in closely packed metals, we focused our analysis on B/C/N interstitials in FCC and HCP metals. The formation energies of B/C/N interstitials in the TMs were calculated, and they were found to exhibit a peculiar behavior common for metals in different rows of the periodic table, which originates from an interplay between the unit cell volume and filling of the d-shell electronic states of the host metals. We further assess the vibrational and electronic entropic contributions to the solubility, as well as the effects of thermal expansion of the metal.

Our calculations were performed within the framework of the density functional theory (DFT) as implemented in the VASP code. We used the generalized gradient approximation (PBE) for the exchange-correlation (XC) functional and projector augmented wave potentials, with a plane-wave energy cutoff of 400 eV. The dependence of on strain was also studied using the PBEsol XC functional. The bulk metals supercells composed of 180 atoms were used, and the Brillouin zone was sampled with 4 × 4 × 4 k-point meshes for FCC and HCP metals. The results of simulations were also selectively checked by larger supercells with up to 630 atoms, and it was found that the results were converged with respect to the system size within 2–3%. Supporting Information Figure S1. The climbing-image nudged-elastic-band method was used for calculating the diffusion barriers. The electronic part of the free energy was calculated in supercells using a 4 × 4 × 4 k-point mesh. The vibrational free energy was calculated by means of the direct method in a 108 atom supercell, using the Phonopy program to generate the necessary displacement and force constant matrices.

where is the total energy of a metal supercell with the interstitial, without impurity atom, and is the chemical potential of the interstitial atom in the reference compound: graphene, bulk α phase, and dimer for C, B, and N atoms, respectively. The details of

Figure 1. (a–c) Formation energies of interstitials in 3d, 4d, and 5d transition metals for boron, carbon, and nitrogen (panels a, b, and c, respectively). The insets show interstitials in the octahedral and tetrahedral positions in the FCC (inset in panel a) and HCP (panel b) metals. The yellow spheres represent interstitial atoms. Only lowest energy configurations are shown (either octa or tetra). (d) Volume per atom for the metals.
chemical potential calculations are given in the Supporting Information. Physically, \( E_f \) is the energy penalty for taking an atom from the reference material being in the thermodynamic equilibrium with the metal and placing it inside the metal. The choice of \( \mu_I \) is not unique, and if, for example, carbides or borides can be formed, the corresponding chemical potentials can be chosen. The values of \( E_f \) we report can, in such cases, easily be recalculated for all the metals by changing \( \mu_I \). Negative values normally point toward the propensity of the metal to form compounds, that is, borides, carbides, and nitrides. \( n(T) \) can then be evaluated through

\[
n(T) = A \exp(-E_f/k_B T)
\]

where \( A \) is a prefactor to be discussed below.

Figure 1(a–c) presents \( E_f \) of B, C, and N interstitials in 3d, 4d, and 5d TMs. The results for the lowest energy configurations (normally octahedral) are shown. The energies for all (octa- and tetrahedral positions) configurations are listed in Supporting Information Figure S3. It is evident that for all the metals considered, the dependence of \( E_f \) on the number of d electrons (or equivalently, position of the metal in the corresponding row in the periodic table) is qualitatively the same: \( E_f \) first increases, then drops and reaches a minimum, then increases again for the coinage metals. The initial growth in \( E_f \) can be associated with the decrease in the volume per atom in the metal, that is, simply lesser amount of open space available for interstitial accommodation. The trend is then reversed, as bonding between the interstitial and metal atoms becomes stronger, as also manifested in a smaller increase in the separation between the neighboring metal atoms upon insertion of the interstitial (Supporting Information Figure S4). Stronger bonding follows from a larger overlap of the d states of the metal and interstitial p states (Supporting Information Figure S5). For coinage metals with fully filled d shells there is essentially no bonding (as also evident from a weak interaction of adatoms with the (111) surface of these metals, Supporting Information Figure S6), so that \( E_f \) is high in spite of a larger volume per atom. For C, our values of \( E_f \) are in agreement with the results of other calculations, but as much smaller simulation cells were used in previous works, giving rise to spurious defect–defect interactions and somewhat overestimated \( E_f \).

Putting aside the uncertainty in the experimental data, in order to correlate our results with the experiments, we evaluated interstitial formation energies using the experimental values\(^{18,20}\) of effective eutectic solubility of C atoms in solid TMAs at \( T = 1000 \) °C, Figure 2. A prefactor of \( A = 100 \) (a typical value to account for anharmonic and other effects to be discussed later) in eq 2 was used. The trends in the calculated values of \( E_f \) proved to be in a striking agreement with the values derived from the experimental data, but the values were smaller, which may be associated with grain boundaries and other extended defects, as discussed below.

The migration barriers \( E_m \) of B/C/N interstitials are presented in Figure 3, along with typical energy profiles along the migration paths, Figure 3d, which are essentially straight lines between the high-symmetry positions, Supporting Information Figure S8. Overall, \( E_m \) decreases with d-shell filling, especially for the late TMs, as volume per atom increases. There is a local maximum close to the metals with the smallest volume per atom (such as Ir or Rh), though. Barriers between some other configurations are presented in Supporting Information Figure S7. Relatively high values of \( E_m \) for some metals may affect the kinetics of foreign species uptake during the growth and should be considered when selecting the substrate.

We also assessed the electronic \( E_{el} \) and vibrational (phonon) \( E_{ph} \) contributions to the formation energy of the interstitials for several metals

\[
\Delta F_{el} = F_{el}[I] - F_{el}[0] - F_{el}[^{\mu}I]
\]

\[
\Delta F_{ph} = F_{ph}[I] - F_{ph}[0] - F_{ph}[^{\mu}I]
\]

which are the differences in electron and phonon free energies of the metal with/without interstitial and that of the reference system for the interstitial atom. Note that all the physical quantities in eqs 3 and 4 depend on \( T \).

The electronic entropy contribution to the formation free energy from the partial occupancy near the Fermi level at finite temperature was found to be small, below 0.3 eV for temperatures up to 1000 K in all cases investigated (Supporting Information Figure S9). As expected, the highest value was obtained for Pd (see Figure 4), which is known for its very large DOS at the Fermi level. This indicates that it is justified to treat 0.3 eV as an upper limit, and a value of about 0.1 eV as being a good estimate for the error introduced by neglecting this temperature dependence.

To estimate the effects of lattice vibrations on the formation free energy of interstitials, calculations in the harmonic approximation at fixed volume were carried out for the case of C in Cu and Rh, using a methodology similar to that of Glensk et al.\(^{38,40,61}\) The temperature dependent phonon contribution to the free energy of interstitial formation as a function of temperature is shown in Figure 4, demonstrating that this contribution is small, approximately \( -0.2 \) eV at 1000 K. Thus, we arrive at 0.2 eV as a reasonable estimate for the error bar of the free energy coming from electronic and vibrational entropy contributions, which corresponds to \( \pm 1 \) order of magnitude difference in solubilities at 1000 °C. Given the fact that the range of the calculated values of \( E_f \) is several electronvolts, we may safely conclude that the dominant contribution to the systematic differences between elements...
stems from this quantity and that vibrational and electronic 
temperature effects are small. In order to get additional insights 
into the effects of volume per atom for interstitial diffusion and 
migration, and also keeping in mind recent experimental results \(^{12}\) reporting the 
dependence of solubility on strain, we further studied the 
effects of external strain \(\epsilon\) on \(E_f\) and, thus, solubility. Figure 5 
shows interstitial formation energies for Cu (a), Ir (b), and Pt 
(c) in the octahedral and tetrahedral positions as functions of 
strain. \(E_f\) decreases linearly with strain, that is

\[
E_f(\epsilon) = E_f(\epsilon=0) - b\epsilon
\]

where \(b\) is a metal-specific constant. We carried out such 
calculations for all the TMs we studied, and the values of \(b\) are 
listed in Supporting Information Table S1. Our results indicate 
that additional control over the growth of 2D materials is 
possible through external strain or substrate thickness for a 
wide range of metals.

To assess the role of exchange-correlation functionals (XCF), 
which may give rise to somewhat different unit cell sizes of 
metals, we tested here the PBE results (this XCF tends to 
overestimate the lattice constant) with PBEsol, generally more

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure3.png}
\caption{Migration barriers of interstitials in 3d, 4d, and 5d transition metals for boron, carbon, and nitrogen (panels a, b, and c, respectively). Typical variations in the energy along the migration paths are illustrated for N interstitials in Ir and Pd, panel d.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Electronic (dashed lines) and vibrational (full thick lines) contributions to the formation free energies of a carbon interstitial in Cu (red) and Rh (blue). Also shown is the anomalously large free energy contribution for Pd (dashed black line).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Interstitial formation energies for Cu (a), Ir (b), and Pt (c) in the octahedral and tetrahedral positions as functions of strain. The results for the tetrahedral interstitials in Cu are not presented as the energy of this configuration is much higher than that for the octahedral interstitials. Two exchange and correlation functionals were used. Note a quick decrease in the formation energies with strain.}
\end{figure}
accurate for solids. The behavior proved to be the same (the difference did not exceed 10%).

The evaluation of $E_f$ as a function of strain also allowed us to estimate a long-range part of the anharmonic vibrational contribution to the free energy of the system, associated with thermal expansion. This should be substantial at $T \sim 1000$ °C, typical temperatures used in the CVD growth of 2D materials, as expansion provides more space to accommodate the interstitial atoms. Thermal expansion of the metal $\epsilon = aT$, where $a$ is the thermal expansion coefficient, gives rise to a dependence of $E_f$ on $T$, so that eq 5 can be written as

$$E_f(T) = E_f(T=0) - abT$$

Rather than carrying out calculations at finite temperature and volume corresponding to the thermally expanded crystal, we computed $E_f$ at $T=0$ and introduced a metal-dependent correction, which is linearly proportional to $T$. Correspondingly, solubility, that is equilibrium concentration of interstitials at temperature $T$ with account for anharmonic effects is

$$n_i(T) = A_f e^{\theta \epsilon / k_B} \times e^{-[E_f(T) + \Delta \eta(T)]/k_BT}$$

where $A_f$ is the geometry factor, $k_B$ is the Boltzmann constant. Values of $\theta / k_B \sim 10^3$ for all the metals are listed in Supporting Information Table S1.

Comparison of our results to the available experimental data, for C, as summarized in Figure 2, indicates a very good agreement between the calculated and experimental solubility trends, but the experimental values of $E_f$ are lower than the theoretical ones. This evidences that some additional, much lower, component to $E_f$ should be present in the experimental values, leading to higher measured solubility. We suggest that grain boundaries and other extended defects are responsible for this behavior, because they provide sites in the sample where the solubility can be expected to be governed primarily by defect morphology, rather than the chemical interaction with the interstitial impurity, thus providing the observed constant damping of the trends. We note that $E_f$ for self-interstitials in grain boundaries of about 2 eV lower than in the bulk has been calculated for Cu. As for solubility of B in TMs, our simulations indicate that it is highest in Pd, then it decreases in Pt, Ni, Co, in agreement with the experimental data. The uptake of B/C/N atoms may also be affected by other impurities (like ubiquitous hydrogen and oxygen atoms) and the measurement techniques used. Thus, our data should set the theoretical limits on the solubility in perfect crystals and, with account for strain/pressure dependence, make it possible to assess it in nanoscale metal crystals. Moreover, the calculated values of solubility and mobility of B/C/N species in TMs should be indispensable for understanding which growth mechanism—precipitation on the metal surface after decrease in temperature or surface diffusion—dominates under specific growth conditions and for providing quantitative data for atomistic models of graphene and mixed BCN materials growth.

To summarize, using first-principles calculations, we showed that the formation energy of B/C/N interstitials exhibits a peculiar but common behavior for d metals in different rows of the periodic table, which originates from an interplay between the unit cell volume and filling of d-shell electronic states of the metals, in agreement with the available experimental data. We further assessed the vibrational and electronic entropic contributions to the solubility, as well as the role of anharmonic effects. Finally, we calculated the migration barriers, which may govern the kinetics of the growth of BCN materials on top of the metals. Our results not only unravel the fundamental behavior of interstitials in TMs but also provide a large body of reference data which can be used for optimizing the growth of 2D materials.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b01377.

Details of calculations and additional results. (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


Supplementary Information to "Solubility of Boron, Carbon and Nitrogen in Transition Metals: Getting Insight into Trends from First-Principles Calculations"

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I. EQUILIBRIUM CONCENTRATION OF INTERSTITIALS IN METALS FROM
CONVENTIONAL SIMULATIONS

In the dilute limit, the equilibrium concentration $n$ of foreign interstitials in solids at
temperature $T$ (assuming that the external pressure $p$ is zero) is normally evaluated through

$$n(T) = A_g \exp(-E_f/k_B T),$$  \hspace{1cm} (1)

where $A_g$ is the geometry factor, $k_B$ is the Boltzmann constant and formation energy of the
interstitial $E_f$ is defined as

$$E_f = E_{tot}[I] - E_{tot}[0] - \mu_I.$$  \hspace{1cm} (2)

Here $E_{tot}[I]$ and $E_{tot}[0]$ are the total energy of the system (at $T = 0$) with and without
the interstitial atom, respectively, and $\mu_I$ is the chemical potential of the interstitial atom
in the reference material (e.g., graphene in case of carbon interstitials, $N_2$ molecule for
nitrogen, etc.). It is assumed that the system (the host material for the interstitial) is in the
thermodynamic equilibrium with the reference system. As we study interstitials in metals,
the charge state of the interstitial is assumed to always be zero, contrary to the case of
semiconductors and insulator[1]. For octahedral and tetrahedral interstitials in FCC and
HCP metals $A_g = 1$ and 2 respectively.

Eq. 1 reflects the balance of the configurational part of the entropy, which lowers the free
energy of the system, and the cost of defect creation. It is assumed that $E_f$ is independent
of $T$ and the electronic and vibrational contributions to the entropy can be neglected. When
the formation energy of the defects (vacancy or interstitial) is high and temperature is low,
Eq. 1 normally gives the qualitatively and even quantitatively correct concentration as a
function of $T$, and makes it possible to determine $E_f$ from measuring the concentration of
impurities at several temperatures. However, this approach may give rise to errors, especially
at high temperatures [2], when anharmonic effects become substantial.

II. CONCENTRATION OF INTERSTITIALS FROM THE GIBBS ENERGY

In a more accurate approach,

$$n(T) = A_g \exp(-\Delta G_f/k_B T),$$  \hspace{1cm} (3)
where Gibbs energy difference $\Delta G_f$ is defined as

$$\Delta G_f(P, T) = F(\Omega_I, T) - F(\Omega_0, T) + PV_f - \mu_I(T).$$  

Here $\Omega_I$ and $\Omega_0$ are the volumes of the system with and without interstitial, $P$ is external pressure, $V_f = \Omega_I - \Omega_0$, $F(\Omega_I, T)$ and $F(\Omega_0, T)$ are the free energies of the system with and without the interstitial, and $\mu_I(T)$ is the free energy per atoms in the reference system.

$\Delta G_f(P, T)$ can be evaluated directly [2] by carrying out DFT molecular dynamics simulations, which come at a high computational cost. Without account for the anharmonic effects, free energy $F$ can be expressed as

$$F(\Omega, T) = E_{\text{tot}}(\Omega) - T [S_{\text{el}}(T) + S_{\text{ph}}(T)],$$

where $S_{\text{el}}$ and $S_{\text{ph}}$ are the electronic and phononic contributions to the full entropy, respectively.

$$S_{\text{el}}(T) = -k_B \sum_i [(1 - f_i) \ln(1 - f_i) + f_i \ln f_i],$$

where the sum runs over all electronic states with energies $\epsilon_i$ and $f_i(\epsilon_i, T)$ is the Fermi-Dirac occupation functions of energy levels $\epsilon_i$.

In the harmonic approximation, $S_{\text{ph}}$ can be calculated, as usual, by finding the eigenvalues of the dynamical matrix [1, 3] and evaluating the harmonic free energy.

At atmospheric (essentially zero) pressure and without account for anharmonicity, Eq. 4 can be reduced to

$$\Delta G_f(P_{\text{atm}}, T) = E_f - T [\Delta S_{\text{el}}(T) + \Delta S_{\text{ph}}(T)],$$

where it is assumed that the supercell is sufficiently large so that at atmospheric pressure the term $PV_f$ is small, $E_f = E_f(T = 0)$ is described through Eq. 2 and

$$\Delta S_{\text{el}} = S_{\text{el}}[I] - S_{\text{el}}[0] - S_{\text{el}}[\mu];$$

$$\Delta S_{\text{ph}} = S_{\text{ph}}[I] - S_{\text{ph}}[0] - S_{\text{ph}}[\mu]$$

are the differences in the electron and phonon entropies of the metal with/without interstitial and that of the reference system for the interstitial atom. Note that all terms in Eqs. 8, 9 depend on temperature.

For the sake of direct comparison of the configurational, electronic, and quasiharmonic contributions to the Gibbs energy at a given temperature, Eq. 7 can also be written as

$$\Delta G_f(P_{\text{atm}}, T) = E_f - \Delta F_{\text{el}}(T) - \Delta F_{\text{ph}}(T),$$

where $\Delta F_{\text{el}} = T \Delta S_{\text{el}}$, and $\Delta F_{\text{ph}} = T \Delta S_{\text{ph}}$.

However, at $T \sim 1000^\circ$C one can expect a considerable thermal expansion of the metal due to anharmonic effects, which should naturally provide more space to accommodate the interstitial atoms, while $E_f$ is calculated at zero temperature and equilibrium (at $T = 0$) volume. As our simulations indicate, $E_f$ linearly depends on volume of the system, or correspondingly, mechanical strain $\epsilon$ (at small strains of a few percent)

$$E_f(\epsilon) = E_f|_{(\epsilon=0)} - b\epsilon,$$

where $b$ is a constant specific to each metal.
With account for thermal expansion of the metal,

$$\epsilon = aT,$$

(12)

where $a$ is the thermal expansion coefficient, the 'anharmonic' formation energy $E_f^a$ can be written as

$$E_f^a = E_f(T=0) - abT,$$

(13)

and the equilibrium concentration $n_a(T)$ of interstitials at temperature $T$ (which accounts for anharmonic effects within the approximations used) is

$$n_a(T) = A_g e^{ab/k_B} x e^{-[E_f - \Delta F_{el}(T) - \Delta F_{ph}(T)]/k_B T},$$

(14)

FIG. S1. Formation energies for carbon and nitrogen interstitials in Cu illustrating the convergence of the results with respect to the simulation supercell size or correspondingly, number of atoms in the supercell.

III. TECHNICAL DETAILS OF CALCULATIONS

The computational accuracy required for a carbon interstitial impurity in Cu is rather higher than for a Cu mono vacancy, as shown in Figure S2b, where the same settings as in Figure S2a are used to calculate the difference in energy between a 108 atom supercell with and without a carbon interstitial. Convergence and necessary settings for relevant technical parameters for the vibrational free energy contribution are shown in Figure S2. We first note in Figure S2a that it is necessary to evaluate the PAW projector functions in reciprocal space (the \texttt{LREAL=False} setting in VASP), rather than the faster but less accurate real-space option (the \texttt{LREAL=Auto}) and that the convergence criterion for the self-consistent field cycle
needs to be set as low as $10^{-9}$ eV for the change in total energy. Figure S2b demonstrates that it is sufficient to use a 600 eV basis set cutoff and a $6 \times 6 \times 6$ k-point mesh is converged to within 10 meV per impurity. Whether semicore states where used or not was found to be irrelevant for the electronic part of the free energy, but for the vibrational properties the effect is more pronounced, as is also shown in Figure S2B. It is also evident from Figure S2A that a vacancy is insensitive to this choice, but in case of the interstitial the atoms are much more closely spaced near the defect, so that the semicore states starts affecting the result. For the case of C in Cu shown here, the effect is still rather small, 50 meV/impurity at 1000 K, but it is expected to increase as we move to the left in the periodic table and the semicore states gradually move higher in energy and become more delocalized.

Chemical potentials of the C, B and N atoms were calculated to be -9.22 eV, -6.68 eV and -8.32 eV, respectively, with the reference compounds being graphene, bulk α B phase and N$_2$ dimer. For graphene, the chemical potential was calculated for the 2-atom unit cell in a periodic setup in the transverse direction, with the separation between the images of graphene sheet of 15Å. The alpha rhombohedral phase of boron had 12 atoms in the unit cell. Isolated nitrogen molecule was put into a cubic supercell with dimensions of $15 \times 15 \times 15$Å. The chemical potentials (computed as the total energy of the system divided by the number of atoms) were converged within 1 meV with respect to the plane wave cutoff energy and the number of K-points (except for nitrogen molecule, of course).

![FIG. S2. Comparison of technical settings for a C interstitial impurity in Cu. (A) Illustrating the importance of evaluating the PAW projectors in reciprocal space (LREAL=.False.) and of a sufficiently tight self-consistent field convergence for the electronic structure. (B) The dependence on the PAW potential used, basis set cutoff convergence and k-point convergence.](image)
IV. REFERENCES


V. ADDITIONAL RESULTS OF CALCULATIONS
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TABLE S1. Strain factors, $b$, and thermal expansion coefficients, $\alpha$, used to estimate anharmonic effects on the solubility. Values of $\alpha$ are given for temperatures of 300 K and 1000 K. An average value is also given for intermediate temperature range.
FIG. S3. Boron, carbon and nitrogen interstitial formation energies in octahedral and tetrahedral configurations for 3d, 4d and 5d transition metals. Electronic configurations of the metals and metal atomic radii are also shown.

FIG. S4. Increase $\Delta a = a - a_0$ in the separation between the metal atoms neighboring the interstitial after insertion of a B/C/N interstitial (panels (a), (b), and (c) respectively).
FIG. S5. (a-e) Local density of states (LDOS) of interstitial C atom, a metal atom neighboring the interstitial (nearest atom) and an atom in the metal far away from the interstitial (bulk) projected on 2p orbitals for carbon and 4d-orbitals for 4d-metals (Tc, Ru, Rh, Pd, Ag). The sharp peak at energies about -7 eV is responsible for bonding between the interstitial and metal atoms. Note that the peak is not present in metal without the interstitial atom. Carbon 2p LDOS integrated over the peak area is presented in panel (f). The 'strength' of bonding can be associated with the value of the integrated LDOS. Zero energy corresponds to the Fermi level in each plot.
FIG. S6. (a-e) Local density of states (LDOS) of C atoms adsorbed on (111) surfaces of 4d metals in the hcp positions, as sketched in panel (f), a metal atom neighboring the interstitial (nearest atom) and an atom in the metal far away from the interstitial (bulk) projected on 2p orbitals for carbon and 4d-orbitals for 4d-metals (Tc, Ru, Rh, Pd, Ag). Note that there is no sharp 2p peak in C LDOS below the 4d metal band, or it is much weaker and overlaps partially with the 4d LDOS at the nearest metal atom. Panel (f) shows the adatom formation energy defined as the energy required to dissociate graphene and put a C adatom on the surface.
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**FIG. S7.** Migration barriers for boron, carbon and nitrogen interstitial between octahedral and tetrahedral configurations for 3d, 4d and 5d transition metals. Electronic configurations of the metals and metal atomic radii are also shown. Symbols \( \triangleleft \) indicate that essentially there is no barrier for the transition from the tetrahedral to the octahedral site. Symbols \( \bigcirc \) indicate that the position of the interstitial is not exactly in the tetrahedral site, so that the migration path is different from what is shown in Fig. S8. Symbols \( \times \) mean that these cases were not considered due to much higher energies of the interstitials in the corresponding sites.
FIG. S8. Migration paths of interstitials from octahedral to octahedral positions in FCC metals (a), from octahedral to tetrahedral positions in FCC metals (b), from tetrahedral to tetrahedral positions in FCC metals (c). Migration paths of interstitials from octahedral to octahedral positions (note: two inequivalent positions) in HCP metals (d), and from tetrahedral to octahedral positions in HCP metals (e).
FIG. S9. The electronic parts of the formation free energies ($F_{el}^{f} = TS_{el}(T)$) for carbon interstitials in coinage metals and Pd, Pt and Rh. The electronic entropy is seen to be negligible in all cases except for Pd and Pt, due to their exceptionally high density of states near the Fermi level. Pd has the highest Pauli susceptibility of any element, which gives us an estimated upper limit of the electronic free energy contribution of 0.3 eV, but with a typical value about one order of magnitude lower.