Effect of N, C, and B interstitials on the structural and magnetic properties of alloys with Cu₃Au structure

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(Received 3 January 2020; accepted 25 March 2020; published 6 May 2020)

High-throughput density functional calculations are used to investigate the effect of interstitial B, C, and N atoms on 21 alloys reported to crystallize in the cubic Cu₃Au structure. It is shown that the interstitials can have a significant impact on the magnetocrystalline anisotropy energy (MAE), the thermodynamic stability, and the magnetic ground-state structure, making these alloys interesting for hard magnetic, magnetocaloric, and other applications. For 29 alloy-interstitial combinations the formation of stable alloys with interstitial concentrations above 5% is expected. In Ni₃Mn interstitial N induces a tetragonal distortion with substantial uniaxial MAE for realistic N concentrations. Mn₃XN_x (X = Rh, Ir, Pt, and Sb) compounds are identified as alloys with strong magnetocrystalline anisotropy. For Mn₃Ir we find a strong enhancement of the MAE upon N alloying in the most stable collinear ferrimagnetic state as well as in the noncollinear magnetic ground state. Mn₃Ir and Mn₃IrN also show interesting topological transport properties. The effects of N concentration and strain on the magnetic properties are discussed. Further, the huge impact of N on the MAE of Mn₃Ir and a possible impact of interstitial N on amorphous Mn₃Ir, a material that is indispensable in today's data storage devices, are discussed in relation to the electronic structure. For Mn₃Sb, noncollinear, ferrimagnetic, and ferromagnetic states are very close in energy, making this material potentially interesting for magnetocaloric applications. For the investigated Mn alloys and competing phases, the determination of the magnetic ground state is essential for a reliable prediction of the phase stability.

DOI: [10.1103/PhysRevResearch.2.023134](https://doi.org/10.1103/PhysRevResearch.2.023134)

I. INTRODUCTION

Magnetic materials with a large magnetocrystalline anisotropy energy (MAE) are an important component in a wide range of everyday devices. Permanent magnets are used, for example, in hard disks, electromotors, and direct-drive wind turbines. Antiferromagnetic compounds find applications in exchange-biased films for data storage devices and magnetic random access memories and are of interest for spintronics applications [1–3]. Present high-performance magnets like Nd-Fe-B contain a considerable amount of rare-earth elements, which in recent years have been subject to strong price fluctuations. The development of alternative permanent magnets without the use of critical rare-earth elements is therefore highly important [4–6]. Basic requirements for a good permanent magnet material are a large uniaxial MAE, a large saturation magnetization, and a high Curie temperature.

High-throughput calculations in the framework of density-functional theory (DFT) have become an increasingly

important tool for the design of new functional materials in recent years [7,8]. In addition to increased computational resources, this is due to the development of large databases and new concepts like efficient descriptors. A number of studies have focused on the development of improved materials for batteries [9,10], thermoelectrics [11–13], and photovoltaics [14].

For magnetic materials, despite their technological importance, computational high-throughput studies are scarce. Bocarsly *et al.* performed a screening of potential magnetocaloric materials [15], and Elsässer and colleagues performed a screening of potential hard magnetic rare-earth lean compounds [16–18]. Other studies focused on potential rare-earth free permanent magnets [19–22] or the prediction of new magnetic compounds [23–26]. A complete study of the stability, magnetic properties, and MAE of potential new magnetic compounds taking into account competing phases and magnetic structures has not, to the best of our knowledge, been performed up to now.

Theoretical high-throughput descriptions of functional magnetic materials involve different energy scales like Coulomb correlations, exchange interactions, and magnetocrystalline anisotropy. Antiferromagnetic (AF) order can have a strong impact on the total energy and phase stability of Mn alloys [24,27], which are of interest for hard-magnetic [28], magnetocaloric [29], and spintronics applications [2]. The effect of AF interactions on the energetics

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has been explored in high-throughput calculations for certain classes of compounds with known magnetic structure prototypes [24,30,31] and on selected compounds using evolutionary algorithms [25,32] or a symmetry-based prioritization [33]. Complex (noncollinear) structures and nonferromagnetic ground states of competing structures in a phase diagram have not been studied up to now, as the computational effort is easily enlarged by one order of magnitude and, often, suitable magnetic structure prototypes are not known. For the calculation of the MAE, which sets an upper limit to the coercivity, a proper treatment of spin-orbit coupling (SOC) and a high numerical accuracy, especially a careful convergence of k -space integrals, are essential. Rare-earth compounds with localized $4f$ electrons require a careful treatment of Coulomb correlations, where accurate methods suitable for a high-throughput screening still have to be developed. While individual aspects have been carefully addressed in the literature, the complexity of interactions makes a high-throughput prediction of functional magnetic materials still highly demanding.

It has been shown in the literature that interstitials can have a strong impact on the magnetic properties, including the magnetocrystalline anisotropy energy [34–36], the magnetic structure [37], and magnetostructural phase transitions [38,39]. The Cu_3Au structure is one of the most common structure types, with more than 200 reported compounds. Ferromagnetic compounds like Fe_3Pt can exhibit a large magnetization, which makes them interesting for applications in exchange-coupled magnets [40,41]. Due to the cubic symmetry they have, however, only a relatively small MAE. In contrast, antiferromagnetic compounds like Mn_3Ir can exhibit a huge magnetocrystalline anisotropy [42] but have vanishing magnetization. This is used in exchange-biased films, where giant exchange anisotropies are reported [43,44]. Further, Mn-rich alloys of Cu_3Au prototype have attracted attention due to a large magnetostriction [45] and Berry-curvature-related phenomena like a large anomalous Hall effect and a facet-dependent spin Hall effect [46–48].

In this paper, we investigate the effect of interstitial N, C, and B atoms on the stability and magnetic properties of 21 experimentally reported compounds with cubic Cu_3Au structure and the magnetic $3d$ elements Cr, Mn, Fe, Co, and Ni. To identify the magnetic ground state of Mn alloys, the energy of different spin structures with maximal magnetic subgroup symmetry is calculated, which according to Ref. [49] accounts for the majority of measured magnetic structures on the Bilbao Crystallographic Server. This allows us to identify also complex noncollinear (NC) ground states, which are frequently observed in Mn alloys. In total, about 1000 magnetic configurations are probed to obtain reliable energies for alloys relevant for the phase stability of binary and ternary Mn alloy systems related to this study (Fig. 1). Stable interstitial phases are identified taking into account all possible decomposition reactions. We show that interstitials can lead to a strong enhancement of the magnetocrystalline anisotropy energy in these alloys and that high-throughput DFT calculations are able to identify hard magnetic materials even in the presence of complex magnetic interactions.

FIG. 1. (a) Examples for automatically generated initial spin structures: a NC structure and collinear ferrimagnetic structure for Mn_3Ir and a collinear ferrimagnetic structure for Mn_{23}C_6 (from left to right). (b) Total number of (solid blue) and number of NC (hatched blue) magnetic structures calculated for binary and ternary Mn alloys in this work.

II. COMPUTATIONAL DETAILS

Calculations were performed within density-functional theory using an extended version of the high-throughput environment (HTE) [50,51] employing the VASP [52,53] and FPLO [54] codes. For the present investigation, the HTE has been extended for the calculation of magnetic properties such as the investigation of different spin configurations and the calculation of the MAE. Further, an automatic detection of suitable interstitial positions was implemented.

For structure optimizations and the calculation of formation energies the VASP code [52,53] has been used following an approach similar to that in Ref. [51]. For the final results shown here projector augmented-wave pseudopotentials with a cutoff energy $E = 500$ eV and constant density of k points corresponding, e.g., to a k mesh of $14 \times 14 \times 14$ k points in the full Brillouin zone (FBZ) for Mn_3Sb were used. For MAE calculations, the full-potential local-orbital method [54] (FPLO, version 14–49) was used, employing the optimized crystal and (collinear) magnetic structure obtained in the preceding VASP calculations. In the FPLO code, accurate full-potential calculations are combined with the solution of the four-component Kohn-Sham-Dirac equation, which implicitly contains spin-orbit coupling up to all orders.

As a descriptor for hard magnetic alloys the magnetic force theorem with a moderate k mesh (up to $20 \times 20 \times 20$ k points in the FBZ) was used, where starting from a self-consistent scalar relativistic calculation, the MAE is evaluated in one-step calculations as the band energy difference between different magnetization directions. In addition, self-consistent relativistic calculations with up to $32 \times 32 \times 32$ k points in the FBZ were used to check the MAE for hard magnetic alloys identified in this study. Further, the magnetic anisotropy of $\text{Mn}_3\text{Ir}(\text{N})$ and $\text{Mn}_3\text{Pt}(\text{N})$ in the noncollinear ground state was calculated using the VASP code employing the magnetic force

theorem. Here, a cutoff energy $E = 400$ eV and a k mesh of $12 \times 12 \times 12$ k points in the FBZ were used.

The results have been cross-checked with self-consistent calculations, including spin-orbit coupling using a cutoff energy $E = 500$ eV and k meshes of $25 \times 25 \times 25$ k points (Mn_3IrN) and $13 \times 13 \times 13$ k points (Mn_3PtN), showing a convergence of the anisotropy energy of about 1 meV.

The anomalous Hall conductivity (AHC) is determined by using the WANNIERTOOLS code, which is implemented within the framework of tight-binding (TB) models [55]. The maximally localized Wannier function (MLFW) TB models are obtained by using the WANNIER90 code [56]. We considered the s , p , and d orbitals for Mn and Ir atoms, and s plus p orbitals were incorporated for N, resulting in 72 and 80 MLFWs for Mn_3Ir and Mn_3IrN , respectively. To evaluate the AHC, the Berry curvature integration is carried out using a uniform k -point mesh of $401 \times 401 \times 401$, which is expressed as follows [57]:

$$\sigma_{xy} = -\frac{e^2}{h} \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_n f[\epsilon(\mathbf{k}) - \mu] \Omega_{n,xy}(\mathbf{k}), \quad (1)$$

$$\Omega_{n,xy}(\mathbf{k}) = -2\text{Im} \sum_{m \neq n} \frac{\langle \psi_{kn} | v_x | \psi_{km} \rangle \langle \psi_{km} | v_y | \psi_{kn} \rangle}{[\epsilon_m(\mathbf{k}) - \epsilon_n(\mathbf{k})]^2}, \quad (2)$$

where e is elementary charge, μ is the chemical potential, $\psi_{n/m}$ denotes the Bloch wave function with energy eigenvalue $\epsilon_{n/m}$, $v_{x/y}$ is the velocity operator along the Cartesian x/y direction, and $f[\epsilon(\mathbf{k}) - \mu]$ is the Fermi-Dirac distribution function. In this work, the anomalous Nernst coefficient (ANC) α_{xy} is determined by using the Mott relation, where we considered only the derivative of AHC at the Fermi level $d\sigma_{xy}/d\epsilon$, which provides a quantitative measure of the ANC:

$$\alpha_{xy} = -\frac{\pi^2 k_B^2 T}{3e} \frac{d\sigma_{xy}}{d\epsilon} \Big|_{\epsilon=\mu}. \quad (3)$$

Unless otherwise mentioned, the generalized gradient approximation (GGA) in the parametrization of Perdew, Burke, and Ernzerhof [58] was used. For calculations in the local spin density approximation (LSDA), which often provides a better description of the spin magnetic moments for weakly correlated systems, the parametrization of Perdew and Wang [59] is used.

For the detection of suitable interstitial positions, the unit cell is scanned on a discrete mesh (here $24 \times 24 \times 24$ points) for sufficient empty space, taking into account the covalent radii r_j of the atoms as tabulated in the atomic simulation environment (ASE) [60,61]. As a condition for suitable positions for the interstitial I we use $d_{\min} = \min_j [d_{Ij} - s(r_I + r_j)] > 0$ for all neighboring atoms j , where $s = 0.7$ is a scaling factor and d_{Ij} is the distance between the interstitial and the atom j . This approach is similar to the detection of empty spheres used in some electronic structure codes. Preference can be given to high-symmetry positions, which was done for the present calculations. The resulting interstitial positions for the Cu_3Au structure are shown in Fig. 2. The interstitial concentration was varied using $2 \times 2 \times 2$, $1 \times 2 \times 2$, $1 \times 1 \times 2$, and $1 \times 1 \times 1$ supercells with one interstitial position occupied, corresponding to interstitial concentrations of 3.0, 5.9, 11.1, and 20 at.%. An additional slight orthorhombic distortion

FIG. 2. Interstitial positions in the Cu_3Au structure: (a) 1b: $(1/2, 1/2, 1/2)$; (b) 3d: $(0, 0, 1/2)$; and (c) 8g: (x, x, x) , with $x \approx 3/4$. The interstitial positions are highlighted in red.

(2%–5% change in the lattice parameters) of the interstitial supercells was also tested but did not have an effect on the stable interstitial compounds discussed in this paper.

The calculation of convex hulls is based on about 2000 alloys (experimental structures and structures close to the convex hull reported in the Materials Project [62]) for ternary M - X - Z systems ($M = \text{Fe, Co, Ni, Cr}$ and Mn ; $Z = \text{B, C, N}$; X : other element). For the competing phases, the same numerical setup as for the interstitial compounds was used. For compounds with Mn atoms, where antiferromagnetic couplings are to be expected, the magnetic ground state was determined for the parent compounds with Cu_3Au structure and their stable interstitial alloys. To ensure reliable phase diagrams for the Mn systems, the magnetic ground state was also determined for the experimentally reported competing phases and some of the energetically low-lying phases reported in the Materials Project. Depending on the size and symmetry of the cell, we used spin configurations compatible with the maximal magnetic subgroups with propagation vector $\mathbf{q} = (0, 0, 0)$, $(1/2, 1/2, 0)$, $(0, 0, 1/2)$ or, alternatively, an antiferromagnetic coupling of sublattices to probe the magnetic ground state.

In the case of Mn_3Ir with the Cu_3Au prototype this results (after removal of symmetry-equivalent configurations) in three collinear [ferromagnetic (FM), AF, and ferrimagnetic] and one noncollinear initial spin structures for $\mathbf{q} = (0, 0, 0)$, which is sufficient to obtain the experimentally reported ground state. It is noteworthy that the experimentally reported magnetic structure of Mn_3Ir does not have maximal magnetic subgroup symmetry but is compatible with the symmetry of the second generation of maximal subgroups [maximal subgroup $R3m'$ (No. 166.101) of the maximal subgroup $Pm\bar{3}m'$ (No. 221.95)]. Nevertheless, the NC initial structures relax to the correct ground state, which underpins the high efficiency of the approach. We explicitly checked that the second generation of maximal subgroups results in the same magnetic ground state. The AF coupling of sublattices corresponds to the highest-ranked magnetic structures in the prioritization scheme proposed in Ref. [33] and is especially useful when the paramagnetic structure has a relatively large number of inequivalent magnetic atoms N_{AF} , which are allowed to couple AF. The number of possible magnetic configurations at this prioritization level is $2^{N_{\text{AF}}-1}$, which results, for instance, for Mn_7C_3 of the hexagonal Cr_7C_3 prototype (with 56 Mn atoms in the unit cell and $N_{\text{AF}} = 8$), in 128 possible magnetic configurations.

TABLE I. Properties of parent compounds in the Cu_3Au structure. Experimental (a_{exp}) and calculated (a_{GGA}) lattice parameters, the calculated formation energy E_f and distance from the convex hull ΔE_h , and the total magnetic moment M are shown.

Alloy	a_{exp} (Å)	a_{GGA} (Å)	E_f (eV/atom)	ΔE_h (eV/atom)	M (in units of $\mu_B/\text{f.u.}$)
Co_3Al	3.66	3.57	-0.175	0.124	3.86
Co_3Ta	3.65	3.63	-0.241	0.001	0.02
Co_3Ti	3.62	3.60	-0.257	0.000	2.71
Fe_3Ga	3.70	3.66	-0.133	0.000	6.98
Fe_3Ge	3.68	3.63	-0.099	0.010	6.37
Fe_3Pt	3.77	3.73	-0.076	0.041	8.46
Fe_3Sn	3.87	3.82	0.086	0.088	6.94
Mn_3Ir	3.77	3.71	-0.215	0.000	0.01 ^a
Mn_3Pt	3.84	3.74	-0.251	0.000	0.00 ^a
Mn_3Rh	3.81	3.71	-0.142	0.000	0.00 ^a
Mn_3Sb	4.00	3.91	0.076	0.086	0.04 ^a
Ni_3Fe	3.55	3.55	-0.088	0.000	4.72
Ni_3Ga	3.58	3.59	-0.289	0.000	0.79
Ni_3Ge	3.57	3.57	-0.292	0.000	0.05
Ni_3In	3.75	3.75	-0.052	0.045	0.69
Ni_3Mn	3.59	3.56	-0.102	0.000	4.85
Ni_3Si	3.51	3.51	-0.462	0.000	0.04
Ni_3Sn	3.74	3.74	-0.188	0.000	0.06
Pt_3Co	3.83	3.88	-0.061	0.000	2.91
Pt_3Cr	3.88	3.91	-0.254	0.000	2.60
Rh_3Cr	3.79	3.78	-0.122	0.000	1.24

^aNoncollinear magnetic structure.

While this approach does not ensure that the correct magnetic ground state is found in all cases, we believe it should give a reliable basis for the prediction of the phase stability in these systems. For the remaining alloys a ferromagnetic magnetic configuration was assumed.

III. RESULTS OF HIGH-THROUGHPUT SCREENING

A. Parent compounds in the Cu_3Au structure

Table I shows the calculated properties of the 21 parent compounds with Cu_3Au structure. The calculated lattice parameters are in good agreement with the reported experimental values, with the largest deviation of about 2.6% for Mn_3Rh and Mn_3Pt . With the exception of Mn_3Sb and Fe_3Sn the calculated formation energy is negative for all compounds, as expected from the formation of alloys in nature. Mn_3Sb was only recently synthesized by high-pressure synthesis [63], and the Cu_3Au structure of Fe_3Sn was reported in high-pressure studies, whereas the ambient pressure phase is hexagonal, in agreement with our calculations (see the Supplemental Material [64]). For 18 of the 21 compounds the calculated distance from the convex hull ΔE_h is below 50 meV/atom, which was proposed in Ref. [51] as a simple descriptor for potentially stable or metastable alloys in high-throughput calculations. In addition to the above-mentioned Mn_3Sb and Fe_3Sn alloys, only Co_3Al is above this criterion, which shows the largest $\Delta E_h = 124$ meV/atom among the calculated compounds. A Cu_3Au structure of Co_3Al was discussed in the literature but could not be stabilized experimentally [65]. This result is confirmed by our study, where only the Al-rich phases AlCo , Al_5Co_2 , $\text{Al}_{13}\text{Co}_4$, and Al_9Co_2 are found to be stable. A complete list of the alloys relevant for the calculation

of the convex hull in Table I is given in the Supplemental Material [64].

For Ni_3X ($X = \text{Si}, \text{Ge}, \text{Sn}$) and Co_3Ta the Fermi energy lies in a pseudogap or valley of the density of states (DOS; see Fig. 3), resulting in a nonmagnetic or only weakly ferromagnetic ground state despite the presence of the magnetic elements Ni and Co. For Mn_3X ($X = \text{Rh}, \text{Ir}, \text{Pt}$, and Sb) the calculated ground state is noncollinear. The antiferromagnetic coupling of the neighboring Mn atoms cannot be fully satisfied in the Cu_3Au structure, resulting in a frustrated triangular spin structure with compensated magnetic moments; see, for instance, Ref. [42] for a more detailed discussion. For $X = \text{Rh}, \text{Ir}, \text{Pt}$ this result is in agreement with experiment [66,67] and earlier calculations [42]. In the case of Mn_3Pt a transition from a triangular to a collinear AF magnetic structure with a

FIG. 3. Total DOS of Co_3Ta and Ni_3Sn for the experimental lattice parameters calculated with FPLO using GGA.

FIG. 4. Calculated magnetic ground-state structures for (a) MnIr and (b) Mn₃Ir. Note that the spin-quantization axis has been rotated to match the results of calculations with SOC. (c) Calculated formation energies for experimental (solid symbols) and hypothetical (open symbols) lattice structures of Mn-Ir alloys for (i) the magnetic ground states (HTE) and (ii) assumed ferromagnetic structures: our calculations (HTE-FM) and data from the Materials Project (MP) and the Open Quantum Materials Database (OQMD). Convex hulls (lines) connect stable structures for the respective methods.

doubled unit cell along c was observed around 365 K in neutron scattering experiments [66], while a similar transition was not observed for Mn₃Rh and Mn₃Ir. For Mn₃Sb, the energies of NC, ferrimagnetic, and FM magnetic structures are within less than 35 meV/atom. Experimentally, a collinear magnetic structure with almost compensating Mn magnetic moments was deduced from neutron scattering experiments [68], while more recent Mössbauer studies suggest a triangular magnetic structure [69].

The energy difference ΔE_{FM} between the magnetic ground state and a ferromagnetic state can be as large as 243 meV/atom for Mn₃Pt. For some of the competing phases the calculated ΔE_{FM} is of similar magnitude, while ΔE_{FM} is trivially zero for compounds with a ferromagnetic ground state. The magnetic structure can thus have a deep impact on the calculated phase stability, going beyond typical effects due to finite temperature. This is exemplarily shown in Fig. 4 for binary Mn-Ir alloys. Assuming a ferromagnetic spin alignment, a hexagonal MnIr₃ phase, $L1_0$ MnIr, and a hexagonal Mn₃Ir phase are on or nearly on the convex hull, in good agreement with results obtained from the Materials Project [62] and the Open Quantum Materials Database [70]. In contrast, calculations with the magnetic ground state yield the experimentally observed $L1_0$ MnIr and Cu₃Au structure of Mn₃Ir as stable phases on the convex hull. For $L1_0$ MnIr and Cu₃Au-Mn₃Ir the magnetic ground-state search resulted in a collinear AF and a NC triangular AF structure, respectively, in agreement with experiment [67,71]. This is accompanied by a significant lowering of the formation energy of nearly 0.2 meV/atom. In contrast, the magnetic ground-state search

FIG. 5. (a) Maximum energy difference $\Delta E_{\text{max}} = \max(E_i - E_j)$ between different magnetization directions versus total magnetic moment M . (b) Maximal change in the ratio of lattice parameters $\delta = \max(a_i/a_j)$ versus change in the formation energy ΔE_f . Data are shown for parent compounds in the Cu₃Au structure (solid black squares) and interstitial structures with B (red), C (blue), and N (green). The interstitial 1b, 3d, and 8g positions are marked with solid squares, circles, and triangles, respectively.

for the two (experimentally not observed) hexagonal phases did not have an effect on the calculated formation energy. An impact of the magnetic structure on the calculated phase stability similar to that for Mn-Ir is found also in other Mn alloy systems and will be discussed in more detail elsewhere.

B. Effect of interstitials on structural and magnetic properties

Figure 5(a) shows the calculated MAE (maximum energy difference between magnetization directions [001], [010], [100], [110], and [111]) for the Cu₃Au parent compounds and interstitial alloys with one N, C, or B atom per f.u., assuming a ferromagnetic alignment of the spins. It can be seen that interstitials can induce huge MAEs up to about 2 meV/atom, one to two orders higher in magnitude than in their cubic parent compounds. N, C, and B are similarly efficient in inducing these large MAEs. The largest MAEs are calculated for the 3d interstitial position, which leads to a tetragonal distortion of the lattice and therefore is promising to achieve uniaxial MAEs. There can be also a significant MAE between the [001], [110], and [111] directions of up to about 0.2 meV/atom for the cubic compounds with heavy 5d

TABLE II. Interstitial alloys with a distance from the convex hull $\Delta E_h < 50$ meV/atom. The parent compound with the Cu_3Au structure, the interstitial atom and position, and the highest interstitial concentration c_{max} with $\Delta E_h < 50$ meV/atom (with three different values of the interstitial concentrations: 5.9, 11.1, and 20) in atomic percent are shown along with the calculated formation energy E_f , ΔE_h , and the total magnetic moment M per atom.

Parent	Interstitial	c_{max}	E_f (eV/atom)	ΔE_h (eV/atom)	M (in units of μ_B/atom)
Co_3Al	C <i>1b</i>	20.0	-0.230	0.010	0.00
Co_3Ta	B <i>1b</i>	11.1	-0.272	0.044	0.00
Co_3Ta	C <i>1b</i>	11.1	-0.211	0.035	0.00
Co_3Ti	B <i>1b</i>	11.1	-0.324	0.043	0.31
Co_3Ti	C <i>1b</i>	11.1	-0.302	0.003	0.22
Fe_3Ga	B <i>1b</i>	5.9	-0.124	0.047	1.50
Fe_3Ga	C <i>1b</i>	20.0	-0.063	0.044	0.63
Fe_3Ga	N <i>1b</i>	20.0	-0.255	0.016	1.05
Fe_3Ge	N <i>1b</i>	5.9	-0.096	0.040	1.32 ^a
Fe_3Pt	N <i>1b</i>	20.0	-0.263	0.000	1.63
Fe_3Sn	N <i>1b</i>	20.0	-0.104	0.037	1.02
Mn_3Ir	N <i>1b</i>	20.0	-0.359	0.026	0.00 ^b
Mn_3Pt	N <i>1b</i>	20.0	-0.471	0.000	0.00 ^b
Mn_3Rh	N <i>1b</i>	20.0	-0.356	0.000	0.00 ^b
Mn_3Sb	N <i>1b</i>	20.0	-0.226	0.036	0.55 ^a
Ni_3Fe	N <i>3d</i>	5.9	-0.063	0.038	1.05
Ni_3Ga	B <i>1b</i>	5.9	-0.305	0.014	0.00
Ni_3Ga	C <i>1b</i>	5.9	-0.273	0.006	0.00
Ni_3Ga	N <i>1b</i>	11.1	-0.258	0.036	0.00
Ni_3In	B <i>1b</i>	20.0	-0.205	0.049	0.00
Ni_3In	C <i>1b</i>	20.0	-0.040	0.038	0.00
Ni_3In	N <i>1b</i>	20.0	-0.173	0.000	0.00
Ni_3Mn	B <i>1b</i>	5.9	-0.110	0.041	1.09
Ni_3Mn	C <i>1b</i>	5.9	-0.071	0.025	1.08
Ni_3Mn	N <i>3d</i>	11.1	-0.113	0.044	0.95
Ni_3Sn	B <i>1b</i>	5.9	-0.196	0.038	0.00
Ni_3Sn	C <i>1b</i>	5.9	-0.134	0.043	0.00
Ni_3Sn	N <i>1b</i>	11.1	-0.135	0.045	0.00
Pt_3Co	B <i>8g</i>	11.1	-0.069	0.048	0.59

^aAntiferromagnetic or ferrimagnetic structure.

^bNoncollinear magnetic structure.

elements (while the energy difference between [001], [010], and [100] is zero due to symmetry). It should be noted, however, that neither stability nor potential antiferromagnetic spin configurations are considered in this plot. The MAEs shown in Fig. 5 thus rather serve to illustrate the potential of interstitials in inducing large MAEs, while for the majority of the data points an experimental realization will not be possible.

This becomes also clear from Fig. 5(b), which shows the formation energy difference ΔE_f with respect to the Cu_3Au parent compound in relation to the induced structural distortion for different interstitial atoms and positions. For the majority of data points ΔE_f is positive, indicating that the interstitial alloy is unlikely to form, at least at the interstitial concentration of 20 at.% considered in the plot. Further, in most cases the *1b* interstitial position, which does not break the cubic symmetry, is the most stable. In most cases this means that a significant enhancement of the MAE is not expected. Noteworthy exceptions, where the spin structure breaks the cubic symmetry, will be discussed further below. Significant structural distortions are found for the *3d* and *8g* interstitial positions with negative ΔE_f in some cases,

suggesting that the interstitial alloys are likely to form. For the *8g* interstitial position, which is least favorable from geometrical considerations, we often find relaxation to a structure corresponding to the *1b* or *3d* position, which provides a higher volume for the interstitial atom.

C. Stable interstitial phases

Table II lists interstitial alloys, where the distance to the convex hull ΔE_h is below 50 meV/atom for an interstitial concentration of more than 5 at.%, suggesting that a substantial number of interstitial atoms can be incorporated in the parent alloy with Cu_3Au structure. This criterion is matched for 29 parent-interstitial combinations, including known antiperovskites like Mn_3XN ($X = \text{Rh}, \text{Ir}, \text{Pt}, \text{and Sb}$) [45,72], Ni_3InN [73], Fe_3PtN [74], Co_3AlC [75], Fe_3GaN [76], and Fe_3SnN [77]. Only the most stable interstitial position is listed. In some cases more than one interstitial position lowers the formation energy, suggesting a partial occupation of the interstitial sites. This is, for instance, the case for Ni_3Mn , where the N *3d* and *1b* positions are close in energy and both of them fulfill the ΔE_h criterion for 5.9 at.% N concentration.

TABLE III. Stable alloys with large uniaxial MAE = $E_{[001]} - E_{[100]}$. The total magnetic spin moment M and the MAE calculated within GGA and LSDA are listed. A collinear spin arrangement is assumed.

Alloy	Interstitial	$M_{\text{GGA}}/M_{\text{LSDA}}$ (in units of μ_B/atom)	$\text{MAE}_{\text{GGA}}/\text{MAE}_{\text{LSDA}}$ (meV/atom)
Mn ₃ Ir		0.37 ^a /0.30 ^a	−0.19/ −0.43
Mn ₃ IrN	N 1b	0.54 ^a /0.49 ^a	−1.32/ −1.27
Mn ₃ Pt		0.36 ^a /0.32 ^a	−0.09/ −0.11
Mn ₃ PtN	N 1b	0.63 ^a /0.57 ^a	−0.16/ −0.22
Mn ₃ Rh		0.43 ^a /0.37 ^a	−0.10/ −0.12
Mn ₃ RhN	N 1b	0.56 ^a /0.51 ^a	−0.31/ −0.29
Mn ₃ SbN	N 1b	0.55 ^a /0.52 ^a	−0.20/ −0.13
Ni ₃ MnN _{0.5}	N 3d	0.96/0.90	−0.09/ −0.10

^aCompounds with a ferrimagnetic structure.

The largest gain in formation energy with respect to the parent compound $\Delta E_f \approx -0.3$ eV/atom is found for Mn₃SbN, where the “interstitial” alloy [72] was reported more than 20 years before the metastable “parent” alloy Mn₃Sb [63]. For the majority of interstitial alloys, stability is accompanied by a negative ΔE_f . However, even a large negative ΔE_f does not ensure formation of a stable alloy. This is the case, for instance, for Co₃AlN and Co₃TiN, where the distance from the convex hull is 0.3–0.4 eV/atom, despite ΔE_f values of about −0.16 and −0.13 eV/atom, respectively. Conversely, a positive ΔE_f does not prevent the formation of a stable interstitial alloy, as in the case of Fe₃GaC_x.

For the majority of interstitials, the 1b position is energetically preferred. The 3d position, which is especially interesting for hard magnetic applications as it breaks the cubic symmetry and leads to a tetragonal distortion of the lattice, is energetically most preferable for Ni₃FeN_x, Ni₃MnN_x, Co₃TaN_x, and Co₃TiN_x. In all cases substantial MAEs between −0.67 and 1.3 meV/cell are induced for $x = 1$ (20 at.% N). The largest absolute value of 1.3 meV/cell is found for Ni₃MnN, albeit with an easy-plane magnetization. However, for Co₃TaN_x and Co₃TiN_x only a minor number of interstitials is expected to be incorporated due to the formation of extraordinary stable Ta-N and Ti-N phases (see the Supplemental Material [64]). For realistic N concentrations (11 at.% N, $x = 0.5$), Ni₃MnN_x shows a significant uniaxial MAE around −100 $\mu\text{eV}/\text{atom}$, comparable to hcp Co. For Ni₃FeN_x, the MAE is small (≈ 15 $\mu\text{eV}/\text{atom}$) and depends on the choice of supercell.

Table III lists stable alloys with large uniaxial MAE for the most stable collinear magnetic structure obtained in the preceding VASP calculations. For comparison, results obtained within LSDA (employing the same GGA optimized structure) are also shown. For both GGA and LSDA, the listed alloys show a large uniaxial MAE, but the absolute values can differ significantly. While GGA typically yields lattice parameters in better agreement with experiment, the local spin magnetic moments are often better described within LSDA. As the MAE depends on subtle details of the electronic structure, this can have a strong impact on the calculated MAE [78], as is the case here for Mn₃Ir, Mn₃PtN, and Mn₃SbN. According to Table III, Mn₃XN and Mn₃X ($X = \text{Rh, Ir, Pt, and Sb}$) would have a huge potential for application as hard magnets, provided they could be stabilized in a ferrimagnetic structure. The largest MAE of about −1.3 meV/atom is obtained for Mn₃IrN. A comparison with Tables I and II shows, however, that with the exception of Mn₃SbN these large MAEs cannot be readily used in bulk magnets, as the ground state is noncollinear with zero net magnetization. However, the strong MAE could be used in exchange-coupled multilayer structures, where a hard magnetic antiferromagnetic layer is coupled to a soft magnetic layer with large magnetization and high Curie temperature. Moreover, as Mn₃SbN shows, a ferrimagnetic ground state may be induced either by variation of the interstitial concentration or epitaxial strain in a thin film. This will be further explored in Sec. IV.

A comparison of Tables I and II shows some remarkable effects of the interstitials on the magnetic properties. While the ground state of Co₃Al is ferromagnetic, Co₃AlC is found to be nonmagnetic. Similarly, the total magnetic moment of Co₃Ti is strongly reduced by interstitial B, resulting in a nonmagnetic ground state for (unstable) Co₃TiB. On the contrary, Co₃Ta is nonmagnetic, while Co₃TaN would be magnetic if it could be synthesized. This shows that interstitials can be very efficient to tune magnetic transitions, which makes interstitial alloying interesting also for magnetocaloric applications.

IV. DISCUSSION

In the previous section we showed that interstitial atoms can have a strong impact on the stability, magnetic properties, and MAE of compounds. While in principle huge MAEs are possible (see Fig. 5), *stable* compounds with the necessary properties for a good permanent magnet are rare, in line with experimental experience. Among the 63 parent-interstitial combinations investigated in this study, Ni₃MnN_x with $x \approx 0.5$ was identified as a stable ferromagnetic alloy with magnetic properties comparable to hcp Co at reduced cost. Further, Mn₃SbN was identified as a ferrimagnet with large MAE, in agreement with the large magnetostriction observed experimentally in this compound [45]. It can be expected that an extended screening of more parent-interstitial combinations would lead to even more promising candidates for hard magnetic applications.

The most striking observation in this study is, however, the huge MAE in Mn₃XN_x ($X = \text{Rh, Ir, Pt, and Sb}$) and the strong impact of interstitial N on the MAE in these compounds, especially for Mn₃IrN. Figure 6(a) shows the calculated DOS of Mn₃IrN and Mn₃Ir. Interstitial N induces changes in the electronic structure in the range of a few hundred meV, larger than the changes in the electronic structure due to a change in the magnetization direction from the easy [001] axis to the hard [100] axis due to spin-orbit coupling, also shown for comparison in Fig. 6(b). The changes in the electronic structure lead also to a change in the orbital moment anisotropy of Ir ($\Delta\mu_l = 0.046\mu_B$ for Mn₃Ir; $\Delta\mu_l = 0.073\mu_B$ for Mn₃IrN) and Mn ($\Delta\mu_l = 0.052\mu_B$ for Mn₃Ir; $\Delta\mu_l = -0.085\mu_B$ for Mn₃IrN), which is closely related to the MAE. Thus, interstitial N has an impact on the electronic structure and MAE going far beyond structural distortions, in agreement with earlier investigations [36].

FIG. 6. (a) Comparison of the DOS of ferrimagnetic Mn_3IrN (blue) and ferrimagnetic Mn_3Ir (cyan) for the easy [001] axis. (b) Band structure of ferrimagnetic Mn_3IrN for the easy [001] axis (blue) and the hard [100] axis (red). For simplicity c/a in both graphs was set to 1.

Another important observation is that according to our calculations, the N concentration in Mn_3XN_x ($X = \text{Rh}, \text{Ir}, \text{Pt}$) can be varied in the range between 0 and 20 at.%, thus providing an additional tuning parameter for the MAE (see Fig. 7). In all cases the interstitial alloys are on or close to the convex hull, well below the $\Delta E_h < 50$ meV/atom criterion for (meta)stability. However, a triangular spin structure is energetically preferred over the collinear ferrimag-

FIG. 7. Distance from the convex hull ΔE_h versus N concentration for Mn_3XN_x ($X = \text{Rh}, \text{Ir}, \text{Pt}$) (solid symbols: NC, pluses: ferrimagnetic).

FIG. 8. Calculated MAE versus c/a ratio for Mn_3IrN . Results are shown for GGA (solid green circles) and LSDA (solid red squares). The volume was fixed to the GGA optimized bulk value.

netic structure throughout the whole concentration range. For Mn_3RhN_x , where the N 1*b* and 3*d* positions lead to a gain in formation energy, up to about 30 at.% interstitial N can be incorporated into the structure based on the ΔE_h criterion. For these high-N concentrations a ferrimagnetic structure with significant net magnetization around $2\mu_B/\text{f.u.}$ and MAE around -1 meV/f.u. is expected based on our calculations. A partial occupation of the N 1*b* and 3*d* interstitial positions may also explain deviations from an ideal triangular spin structure reported in this compound [72].

Figure 8 shows the calculated MAE as a function of c/a for Mn_3IrN in the ferrimagnetic spin configuration employing self-consistent calculations with an enhanced k mesh. First, we note that the MAE obtained from self-consistent calculations for the bulk value is in good agreement with the MAE obtained with the force theorem in the high-throughput calculations, underlining the suitability of the band anisotropy as a descriptor in high-throughput calculations. The results show that the huge MAE is robust against variations of the c/a ratio in epitaxially grown films, with values between -4 and -8 meV/cell for a wide range of lattice parameters. In particular, the results show that the symmetry breaking due to the ferrimagnetic spin arrangement is responsible for the huge MAE and not a slight distortion of the lattice from cubic symmetry ($c/a = 1$). The total spin moment ranges between $2\mu_B$ and $4\mu_B/\text{cell}$ for the c/a ratios investigated. Thus, Mn_3IrN would be an excellent hard magnetic material if it could be stabilized in the ferrimagnetic spin configuration, which would outperform the known hard magnet $L1_0$ CoPt with an MAE of about 0.5 meV/atom and a total magnetic moment of about $1.1\mu_B/\text{atom}$. According to our VASP calculations, N also has a strong impact on the magnetic anisotropy in the NC ground state and enhances the energy difference $\Delta E = E_{\Gamma^{4g}} - E_{\Gamma^{5g}}$ between the easy Γ^{4g} ground state and the Γ^{5g} representation of the magnetic structure from about -8 meV (Mn_3Ir) to -12 meV (Mn_3IrN). Based on these results we expect that interstitial N also has a strong impact on amorphous Mn_3Ir , which is one of the state-of-the-art

FIG. 9. Calculated band structure and AHC of (a) and (b) Mn_3Ir and (c) and (d) Mn_3IrN , respectively.

materials for providing exchange bias in hard magnetic films. In the case of $\text{Mn}_3\text{Pt(N)}$, ΔE changes sign from -3 meV (Mn_3Pt) to 6 meV (Mn_3PtN), so that the Γ^{5g} representation becomes the ground state.

According to our calculations, a relatively large epitaxial strain around 5% is necessary to stabilize a ferrimagnetic ground state in Mn_3IrN at 0 K (see Fig. 1 in the Supplemental Material [64]). Surprisingly, the necessary strain in Mn_3Ir is lower, despite the smaller energy difference between the NC and ferrimagnetic states in Mn_3IrN , possibly indicating that an intermediate N concentration is the most suitable for a stabilization of the ferrimagnetic state. Further, we note that for the related compound Mn_3GaN calculations by Zemen *et al.* [79] have shown that a combination of strain and temperature leads to a stabilization of a ferrimagnetic ground state. A similar behavior was recently also experimentally observed for a Mn_3NiN film on a SrTiO_3 substrate [80]. In passing we note also that epitaxial strain in Mn_3XN as well as in Mn_3X ($X = \text{Rh}, \text{Ir}, \text{Pt}$) is accompanied by a significant net magnetization in the NC ground state, albeit smaller than the one predicted for Mn_3SnN [81]. This suggests that a piezomagnetic effect may be observed in a wide range of NC antiferromagnets. A more detailed analysis is beyond the scope of the present high-throughput study and left for future experimental and theoretical work.

The AHC and ANC depend on the spin configuration of the system. The origin of nonvanishing AHC in Γ^{4g} magnetic ordering has been studied based on symmetry analysis [82,83]. Figure 9 shows the calculated band structure and AHC of Mn_3Ir and Mn_3IrN in the Γ^{4g} ground state. For both compounds, the calculated AHC σ_{111} is significant, with

315 S/cm for Mn_3Ir and 157 S/cm for Mn_3IrN . This is in overall good agreement with a study by Chen *et al.* in which a moderately smaller AHC was calculated for Mn_3Ir (230 S/cm) [46] but differs in sign and magnitude from a recent AHC calculation by Huyen *et al.* for Mn_3IrN (-573.3 S/cm) [84]. The AHC has been shown to be highly sensitive to the choice of the magnetization direction [83], which may be a reason for this discrepancy. Based on our calculations, we predict a huge anomalous Nernst effect for Mn_3Ir and Mn_3IrN . The calculated ANC α_{111} is 6195 and -4892 S/(cm eV) for Mn_3Ir and Mn_3IrN , respectively, within the range of the best reported antiferromagnetic materials up to now [85–87]. Noteworthy, there is a change in sign of ANC between Mn_3Ir and Mn_3IrN . Both end members of the Mn_3IrN_x ($0 \leq x \leq 1$) series show interesting transport properties. According to our thermodynamic calculations alloys with intermediate N concentrations are stable, which may be a route for further tuning of the transport properties.

V. SUMMARY

In summary we have shown that the interstitial elements N, C, and B can have a strong impact on the magnetic properties of cubic compounds and that interstitial alloying can be a fruitful approach to enhance the magnetic properties. For reliable predictions of materials with enhanced properties, phase stability (i.e., calculation of the convex hull including all possible decomposition reactions) is essential. The high-throughput scheme introduced in this paper is a unique computational tool to identify promising magnetic materials in order to guide the design of new magnetic materials.

Based on our calculations, we expect ferromagnetic Ni_3MnN_x (with about 11 at.% N) and the ferrimagnetic compounds Mn_3SbN and Mn_3RhN_x (with about 30 at.% N) to show bulk magnetic properties with sizable magnetization in the range of $0.5\mu_B$ – $1\mu_B$ /atom and sizable uniaxial MAE in the range of 100–200 $\mu\text{eV}/\text{atom}$.

The $\text{Mn}_3\text{X(N)}$ ($X = \text{Rh}, \text{Ir}, \text{Pt}$, and Sb) compounds are identified as materials with strong MAE and a sizable magnetization in a collinear ferrimagnet state. The calculations also show that, with the exception of Mn_3SbN , these materials cannot readily be used as bulk magnets, as their ground state is a noncollinear fully compensated antiferromagnet. As a strong magnetic anisotropy is also present in the noncollinear ground state of these alloys, these materials are, however, of strong interest for multilayer structures where the hard magnetic antiferromagnetic layer is exchange coupled to a soft magnetic layer with large magnetization. Especially for Mn_3Ir , which is already used as an exchange bias material in hard magnetic films, interstitial alloying with N can be a promising approach to enhance the magnetic properties of a state-of-the-art material. Further, an application of the strong MAE in the ferrimagnetic state may be possible in thin films but requires a more detailed theoretical and experimental investigations. For Mn_3Ir and Mn_3IrN we find a significant anomalous Hall effect and a huge anomalous Nernst effect. Variation of the N concentration may be a route for further

optimization of the topological transport properties, as the Mn_3IrN_x alloys share the same triangular spin arrangement. Moreover, we have shown that interstitials can also have an impact on the ground-state magnetic structure and can thus be used to tune magnetic transitions, for instance, in magnetocaloric applications. In $\text{Mn}_3\text{Sb(N)}$ the magnetic ground state changes from NC to ferrimagnetic upon alloying with N. For Mn_3Sb , NC, ferrimagnetic, and ferromagnetic magnetic states are very close in energy, indicating that moderate fields may be sufficient to switch from a low to a high magnetization state. This makes Mn_3Sb -based alloys potentially interesting for magnetocaloric applications but requires further studies.

For Mn alloys, our calculations show that the assumption of a ferromagnetic spin alignment, which is currently used in high-throughput databases, is unreliable to predict formation energies and phase stability. The symmetry-based methods applied in this paper to determine the magnetic ground state can pave the way to predictions of the phase stability based on DFT high-throughput calculations for these

important alloy systems, which are of interest, e.g., for permanent magnet, magnetocaloric, and spintronics applications.

ACKNOWLEDGMENTS

We acknowledge fruitful discussions with K. G. Sandeman and Z. Gercsi. Financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through CRC/TRR 270, Project ID 405553726; the German federal state of Hessen through its excellence program LOEWE “RESPONSE”; and the European Community (NOVAMAG) is gratefully acknowledged. The work of J.Z. was supported by the Ministry of Education, Youth and Sports of the Czech Republic from the OP RDE program under the project International Mobility of Researchers MSCA-IF at CTU No. CZ.02.2.69/0.0/0.0/18_070/0010457 and from the Large Infrastructures for Research, Experimental Development and Innovations project IT4Innovations National Supercomputing Center-LM2015070. Calculations for this research were conducted on the Lichtenberg high-performance computer of the TU Darmstadt.

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