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Designing rare-earth free permanent magnets in Heusler alloys via interstitial doping

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Abstract

Based on high-throughput density functional theory calculations, we investigated the effects of light interstitial H, B, C, and N atoms on the magnetic properties of cubic Heusler alloys, with the aim to design new rare-earth free permanent magnets. It is observed that the interstitial atoms induce significant tetragonal distortions, leading to 32 candidates with large (> 0.4 MJ/m\textsuperscript{3}) uniaxial magneto-crystalline anisotropy energies (MAEs) and 10 cases with large in-plane MAEs. Detailed analysis following the perturbation theory and chemical bonding reveals the strong MAE originates from the local crystalline distortions and thus the changes of the chemical bonding around the interstitials. This provides a valuable way to tailor the MAEs to obtain competitive permanent magnets, filling the gap between high performance Sm-Co/Nd-Fe-B and widely used ferrite/AlNiCo materials.

Keywords: Permanent magnets, Interstitial, Tetragonal distortion, Magneto-crystalline anisotropy energy

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1. Introduction

Permanent magnets are of great technical importance for many key technologies such as electric vehicles, wind turbines, and automatisation and robotics to name only a few [1]. Looking at the intrinsic magnetic properties, such materials demand a large magneto-crystalline anisotropy energy (MAE), a sizable saturation magnetization, and a high Curie temperature. The MAE originates from the spin-orbit coupling (SOC) and sets an upper limit for the microstructure dependent coercivity of permanent magnets. At present, rare-earth magnets based on Sm-Co (MAE: 17.0 MJ/m$^3$, Magnetization ($M_s$): 910 kA/m) and Nd-Fe-B (MAE: 5.0 MJ/m$^3$, $M_s$: 720 kA/m) are prototypes of high performance permanent magnets, with a substantial cost and performance gap to other classes of commercially available permanent magnets such as AlNiCo (MAE: 0.04 MJ/m$^3$, $M_s$: 50 kA/m) and ferrites (MAE: 0.03 MJ/m$^3$, $M_s$: 125 kA/m) [2]. Thus, there is a great interest to develop novel permanent magnets so that the full spectra of applications can be achieved, ideally without critical elements such as rare-earth elements [3-4].

An enlightening idea was proposed to achieve giant MAE in tetragonally distorted FeCo alloys [5], where both the tetragonal distortion and fine tuning of the number of electrons by alloying are crucial for the enhanced MAE. Follow-up experimental studies on FeCo alloys deposited on various substrates confirmed the theoretical prediction [6]. Nevertheless, due to the strong tendency for the FeCo alloys to relax, it is difficult to maintain the tetragonal distortion induced by the underlying substrates for thin films thicker than 2 nm [6, 7, 8]. Recently, following the prediction based on DFT calculations [9, 10], systematic studies have been performed on FeCo+X (X= C and B), where spontaneous tetragonal distortions with $c/a=1.04$ can be induced by a few atomic percent interstitial doping of C or B atoms occupying the octahedral interstitial sites. The resulting MAE can be as large as 0.5 MJ/m$^3$ with B concentration up to 4 at%, where the tetragonal strain reaches 5%. For Fe$_{0.38}$Co$_{0.62}$, a large interstitial concentration of 9.6 at% B was achieved [10]. The effect of light interstitials on the magnetic
properties of body-centered cubic (BCC) iron has also been well studied. α-
Fe with 12.5 at% content of nitrogen interstitial has been grown by sputtering
on the MgO (100) substrates, leading to about 10% tetragonal distortion and
significant enhancement of magnetization and MAE [11]. First-principle cal-
culations and experimental results show that Fe with nitrogen interstitial has
sizable MAE, favoring perpendicular magnetization [11]. Using the molecular
beam epitaxy, boron has been incorporated into bcc Fe as interstitial dopants,
which give rise to tetragonal distortions but the resulting MAE still favors in-
plane magnetization due to tendency for B atoms to be agglomerated [12], where
the interstitial content of B atoms can be as high as 14 at%.

Considering only the crystal structure, the austenite phase of Heusler alloys
with the conventional cubic cell can be regarded as a $2 \times 2 \times 2$ supercell of the
cubic lattice. In this regard, light interstitials such as H, B, C, and N can also
be promising to induce significant tetragonal distortions and thus substantial
MAE to Heusler alloys, like the FeCo alloys and bcc Fe. It is noted that the
Heusler alloys in the tetragonal martensitic phase do show significant MAE. For
instance, among 286 Heusler compounds, a systematic high throughput (HTP)
screening suggests 19 potential tetragonal systems with large out-of-plane MAE
(as large as 0.9 MJ/m$^3$) [13]. Matsushita et al. found 15 Heusler compounds
have tetragonal distortions of which the MAEs ranges from -12 MJ/m$^3$ to 5.19
MJ/m$^3$ [14]. Focus on Ni based full Heusler compounds, Herper et al. [15] found
tetragonal Ni$_2$FeGe has an MAE of 0.95 MJ/m$^3$, which can be further increased
to 1 to 2 MJ/m$^3$ by non-magnetic doping. Furthermore, imposing strain by
proper substrates is helpful to engineer a large MAE out of the cubic Heusler
alloys. It is found that the out-of-plane MAE of epitaxial Co$_2$MnGa (001) films
can be remarkably enhanced from 0.11 MJ/m$^3$ to 0.33 MJ/m$^3$ by changing
the substrate from ErAs/InGaAs/InP to ScErAs/GaAs [16]. Lastly, previous
experiments have already demonstrated that interstitials can be incorporated
into Heusler alloys, leading to enhanced mechanical stability and magnetocaloric
effect [17, 18]. For Ni$_{43}$Mn$_{46}$Sn$_{11}$C$_x$, when the interstitial content x is increased
from 0 to 8 the martensitic phase transformation temperature is increased from
196 to 249 K, while a remarkable increase of MAE is observed when \( x \) is increased from 0 to 2 \[17\]. Due to large loss of manganese in content of \( x=8 \), there is even a distortion of crystal structure from \( \text{Hg}_2\text{CuTi-type} \) to the \( \text{Cu}_2\text{MnAl-type} \) \[17\].

Similar effect has also been observed in \( \text{Ni}_{50}\text{Mn}_{47.4}\text{In}_{14.2}, \text{Ni}_{43}\text{Mn}_{46}\text{Sn}_{11} \) and \( \text{Ni}_{50}\text{Mn}_{38}\text{Sb}_{12} \) doped with B interstitial \[18, 19, 20\].

In this work, focusing on developing rare-earth free permanent magnets, we have performed high-throughput first-principles calculations to investigate the effects of light interstitials (e.g., H, B, C, and N) on cubic Heusler alloys. After identifying the most favorable site preference of the interstitial atoms, the MAE of compounds with negative formation energy was evaluated to select the most promising candidates. Apart from thermodynamically stable criteria, the disorder effect should also be considered, which is however beyond the scope of the present paper and saved for future study. We observed that the induced MAE can be as large as 2.4 MJ/m\(^3\), and there are 32 systems with a sizable out-of-plane MAE (\( \approx 0.4 \text{ MJ/m}^3 \)). Detailed analysis based on the Bain path and the atom-resolved MAE reveal that not only the global tetragonal distortion but also the associated local chemical bonding are crucial for the interstitial induced magnetic anisotropy.

2. Computational details

Starting with 128 full Heusler alloys with space group \( \text{Fm} \overline{3} \text{m} \) including at least one of magnetic atoms Cr, Mn, Fe, Co, and Ni from the Inorganic Crystal Structure Database (ICSD) \[21\] (cf. Table A.1 in Appendix A), we performed density functional theory (DFT) calculations firstly to identify the energetically most favored interstitial sites for H, B, C, and N atoms. There are four types of interstitial sites based on the symmetries, as shown in Fig 1(a). The DFT calculations are managed with our in-house developed high-throughput environment (HTE) \[22, 23\], using both the Vienna ab initio Simulation Package (VASP) \[24, 25\] and full-potential local-orbital (FPLO) \[26, 27\] codes. The structure optimization is performed in a two step manner. Firstly, ultrasoft
pseudopotentials (US-PP) \cite{28} are used in combination with the PW91 \cite{29} exchange correlation functional, where the cutoff energy for the plane wave basis is set to 250 eV and a k-mesh density of 30Å\(^{-1}\). Secondly, the structure is relaxed using the projector augmented plane wave (PAW) method with the exchange-correlation functional under the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) \cite{30} with increasing plane wave expansion as 350 eV and k-mesh density as 40 Å\(^{-1}\) to achieve good convergence. After obtaining the energy lowest configuration, the MAEs of candidates with negative formation energy are calculated by using FPLO with a k-mesh density of 120 Å\(^{-1}\) to guarantee fine convergence. For the MAE calculations of Ni\(_2\)FeGa with C interstitial, the resulting k−mesh is set as \(24 \times 24 \times 17\). The bonding analysis is done in terms of the crystal orbital Hamilton population (COHP) evaluated using the LOBSTER code \cite{31}.

3. Results and discussions

As shown in Fig. 1(a), the systems we considered correspond to doping 6.25 at% interstitial atoms (I) into the full Heusler alloys (X\(_2\)YZ), leading to a general chemical formula X\(_2\)YZI\(_{1/4}\). This is in accordance with the typical doping concentrations experimentally accomplishable, e.g., 12.5 at% content of N in Fe and 9.6 at% of B in Fe\(_{0.38}\)Co\(_{0.62}\). \cite{10, 11} Like Fe-Co alloys, we find light interstitials can indeed cause stable tetragonal distortion to cubic full Heusler alloys, which is quantized by the c/a ratio between the c-axis and in-plane lattice constants. As shown in Table 1 with N interstitials, Fe\(_2\)NiAl has the a tetragonal distortion as large as c/a=1.57. Such strong tetragonal distortions prevail in the other Heuslers with the other types of interstitial atoms, which break the cubic symmetry and hence lead to possible significant MAE. From the theoretical point of view, the MAE is defined as the total energy difference between the magnetization directions parallel to [100] (in-plane) and [001] (out-of-plane) directions as

\[
\text{MAE} = E_{[100]} - E_{[001]} \quad (1)
\]
where $E_\alpha$ is the total energy when magnetization direction is parallel to $\alpha$. When the MAE value is positive (negative), the spontaneous magnetization will lie in the out-of-plane (in-plane) direction. Nevertheless, not all the interstitials are thermodynamically stable, as indicated by the formation energy. The candidates with an MAE more than 0.4 MJ/m$^3$ and a negative formation energy are listed in Table 1.

We notice all the parent Heusler compounds listed in Table 1 are ferromagnetic apart from Mn$_2$VGa and Rh$_2$NiSn. In our high throughput calculations, for convenience, all Heusler compounds are assumed to be ferromagnetic (FM). Previous studies [32, 33] have shown Rh$_2$MnAl is an antiferromagnet with Mn are antiferromagnetic coupling between nearest neighbors in the (111) plane, which is still in the same antiferromagnetic phase after incorporating C or N interstitials. As to Mn$_2$VGa, experimental research [34] has shown it is a half-metallic ferrimagnet with antiferromagnetic coupling between Mn and V with a total net saturation magnetization per formula unit as 1.88 $\mu_B$ at 5 K. After inducing interstitial (C, B or N), Mn$_2$VGa is still ferrimagnetic with antiferromagnetic coupling between Mn and V, although initial spin configuration is ferromagnetic. Mn$_2$VGa have large MAE values as 1.82 MJ/m$^3$, 1.50 MJ/m$^3$ and 1.26 MJ/m$^3$ with B, C and N interstitial, respectively. However, due to the ferrimagnetic phase, the resulting magnetization densities for Mn$_2$VGa with B, C and N interstitial are as weak as about 0.04-0.05 $\mu_B/\AA^3$. Among all listed compounds in Table 1, Rh$_2$NiSn is weak ferromagnetic as experimental study [35] suggests it has a magnetic moment 0.6 $\mu_B$ per formula unit. Our calculations demonstrate that H interstitials can induce a tetragonal distortion of $c/a=1.26$ and a sizable MAE value as 0.82 MJ/m$^3$, whereas the magnetization is only about 0.02 $\mu_B/\AA^3$.

As shown in Table 1 we found 32 compounds with a large out-of-plane MAE (i.e. 0.4 MJ/m$^3$) as well as 10 compounds with large in-plane MAE (absolute value larger than 0.4 MJ/m$^3$). In general, the interstitial atoms prefer to be located at the octahedral centers (including both the 24f and 24g sites) except for the H interstitials in Au$_2$MnAl which is stable at the tetrahedral center. For the
cases of octahedral center, the interstitials mostly prefers 24f sites ($\frac{1}{2}, 0, 0$) where there are the same atoms in the plane perpendicular to the c-axis. On the other hand, for Co$_2$FeAl with N, Au$_2$MnAl with N and C, Ni$_2$MnSn with B, C and N, interstitials prefer 24g sites ($\frac{1}{2}, \frac{1}{4}, \frac{1}{4}$). We note that Fe$_3$Ge with H interstitial has the largest magnetization density as 0.13 $\mu_B$ /Å$^3$ as well as quite large MAE value (1.50 MJ/m$^3$), indicating it is a promising permanent magnet. Furthermore, comparing with the magnetization and MAE of experimentally realized permanent magnets [1, 36, 37, 38, 39, 40] Heusler alloys with interstitials can fill the gap between the low performance magnets (such as AlNiCo and ferrite) and high performance magnets (such as Sm-Co and Nd-Fe-B) in terms of MAE and magnetization, which can spread a wide spectrum of applications.

Interestingly, Au$_2$MnAl with H is the only candidate where the interstitials prefer the tetrahedral center (16e site). However, for cases of Au$_2$MnAl with N and C, interstitial prefers to be located in the octahedral centers with in-plane MAE. Such special interstitial behaviors can be easily understood based on the chemical bonding. Intuitively, due to the large atomic spheres of Au atoms, there is more space between the tetrahedron edge bound than the other Heusler compound. For instance, in Au$_2$MnAl with H, the bond length of H-Au pair in tetrahedral center (1.83 Å) is comparable with that in octahedral center (1.93 Å). On the other hand, the bond length of Cu-H pair for Cu$_2$MnAl with H in tetrahedral center is just 1.62 Å, of which the value is obviously smaller than the H-Au pair for H interstitial in the tetrahedral center of Au$_2$MnAl (1.83 Å). This suggests Au atom can really provide more space for interstitials in the tetrahedral site. It should be noticed that Cu-H pair in octahedral center also has a bit larger bond length (1.70 Å) than that in tetrahedral center. However, in the tetrahedral center case, the bond length is too small to provide enough space for the interstitials. Thus, the H interstitials prefer the octahedral centers in Cu$_2$MnAl. On the other hand, for Au$_2$MnAl with C and N, it is observed that the interstitial atoms still prefer the octahedral center because of the larger atomic radii of C and N atoms compared to that of H. Therefore, in order to get the interstitials incorporated at the tetrahedral center, two conditions
should be satisfied: (a) The interstitial atoms should be small; (b) There should be large atoms in the parent compound, providing more space. Different site preference of the H and C/N interstitials induces significant changes on the MAE of Au$_2$MnAl, e.g., H-interstitials favor out-of-plane magnetization while C/N interstitials lead to in-plane magnetization.

According to Table 1, Fe$_2$CoGa with interstitials is a promising candidate for permanent magnets. However, in the ICSD database, Fe$_2$CoGa (ICSD ID: 102385 and 197615) and Fe$_2$CoGe (ICSD ID: 52954) are in the full Heusler structure, while early Mössbauer measurements have shown Fe$_2$CoGa and Fe$_2$CoGe are energetically favored in the inverse Heusler structure [41, 42]. Previous theoretical study [43] found that full Heusler Fe$_2$CoGa have a martensitic phase transition with a c/a ratio as 1.4, which is also confirmed by our calculation (cf. Fig. 2(a)). According to our Bain-path calculations, the inverse Heusler structure is still more energetically favored for Fe$_2$CoGa, even after considering H, B, C, and N interstitials. Nevertheless, after introducing interstitials, for the full Heusler structure, the c/a ratio is near to 1.4; whereas for the inverse Heusler structure, the c/a ratio of Fe$_2$CoGa with interstitials is just from 1.1-1.2 due to there is no metastable phase (Fig. 2(a)). The MAE values of the inverse Fe$_2$CoGa with B, C, N, and H interstitial are 0.1026 MJ/m$^3$, 0.2148 MJ/m$^3$, 0.3798 MJ/m$^3$, and 0.1925 MJ/m$^3$, respectively. Such lower MAE values are partially due to that interstitials induce much weaker tetragonal distortion to Fe$_2$CoGa for inverse Heusler structure (1.1 ≤ c/a ≤ 1.2) than that for full Heusler structure (1.45 ≤ c/a ≤ 1.5).

More interestingly, C, N, and H interstitials induce significant MAEs to Ni$_2$FeGa. Experimental studies suggest that Ni$_2$FeGa can be grown by melt-spinning technique [44] or glass-purify method [45], transforming from high chemical ordering L2$_1$ structure (full Heusler) to martensitic structure at 142 K with a high Curie temperature of 430 K [44]. Further experiments showed polycrystalline alloys Ni$_{53+y}$Fe$_{20-x}$Ga$_{27}$ have smaller but comparable entropy changes as classical magnetocaloric Heusler alloy systems Ni-Mn-Ga and Ni-Mn-Sn [46]. DFT calculations suggest that Ni$_2$FeGa has a tetragonal (corresponding
to the martensitic phase) structure of $c/a=1.35$ with an MAE as 0.318 MJ/m$^3$. We also found that Ni$_2$FeGa is stable in the tetragonal structure with a $c/a$ ratio as 1.35 (Fig. 2(b)) and a comparable MAE as 0.2334 MJ/m$^3$ (0.0698 meV per chemical formula cell). However, the energy difference between tetragonal and cubic structures is as small as 2.80 meV/atom. As proposed by Barman, the martensite phase transition temperature is proportional to the energy difference between cubic and martensite phases, as manifested by the experimental martensitic transition at 142 K. After inducing interstitial C, H, or N, Ni$_2$FeGa is stable in the tetragonal phase with $c/a \approx 1.40$. Correspondingly, the MAEs have been enhanced to 1.43 MJ/m$^3$, 0.94 MJ/m$^3$, and 0.56 MJ/m$^3$ for Heusler Ni$_2$FeGa with N, C, and H interstitials, respectively. Obviously, C and N interstitials cause more significant enhancement on the MAE than the H interstitials, though the resulting $c/a$ ratios are comparable. Therefore, we suspect that both the tetragonal distortion and the chemical bonding environment will influence the MAE values for Heusler with interstitial, which will be discussed in detail below.

Turning now to the origin of the induced MAE by interstitials, from the theoretical perspective, beside the shape anisotropy due to the magnetic dipole-dipole interaction, the magneto-crystalline anisotropy (MCA) can be attributed to the spin-orbit coupling (SOC), which is the dominant contribution to MAE and hence coercivity for PMs. Based on the perturbation theory, Bruno pointed out that the MCA can be formulated as

$$MCA = -\sum_i \frac{\xi_i}{4\mu_B} \Delta\mu_i, \quad (2)$$

where $\xi_i$ denotes the atomic SOC constant and $\Delta\mu_i$ is the orbital moment difference between the magnetization directions parallel to [001] and [100] for the $i$-th atom. We note that such a model is best applicable for strong magnets where the majority spin channel is almost fully occupied, whereas there is a more general formula considering the spin-flip and quadruple terms. Taking Ni$_2$FeGa as an example, Table 2 shows the atom-resolved orbital moments and the resulting contributions to the MCA using Bruno’s formula, where the atomic
SOC constants for Ni and Fe are 630 cm\(^{-1}\) (corresponding to 78.1100 meV) and 400 cm\(^{-1}\) (corresponding to 49.5937 meV) taken from Ref. [51]. The resulting MCA for Ni\(_2\)FeGa with C, N, and H interstitials based on the Eq. (2) are 0.316 meV/f.u., 0.528 meV/f.u. and 0.330 meV/f.u., respectively. Correspondingly, the MAEs based on Eq. (1) are 0.296 meV/f.u., 0.439 meV/f.u. and 0.167 meV/f.u., respectively. The relative MAE differences of Bruno’s model to that of Eq. (1) are 17.17%, 23.83% and 79.61%. Nevertheless, the trend is correctly reproduced and we believe the atomic-resolved contributions evaluated based on Eq. 2 are still valuable to elucidate the origin of MCA. It is noteworthy that the tetragonal distortion ratios for Ni\(_2\)FeGa with H, C and N interstitial are 1.39, 1.40 and 1.40, respectively (cf. Table 1). To make a direct comparison to the pristine Ni\(_2\)FeGa, we evaluated the MCA and orbital moments for Ni\(_2\)FeGa without interstitials but with imposed c/a=1.40, resulting in an MCA of 0.066 meV and 0.170 meV per chemical formula by using Eq. (1) and Bruno’s model Eq. (2), respectively. Again, the MAEs obtained from the Bruno’s model can be well compared with that from Eq. (1) for Ni\(_2\)FeGa with C and N interstitial, but not for H interstitial case and parent compound.

The remarkable variation of the orbital moments and the resulting significant enhancement of MCAs can be attributed to the atoms surrounding the interstitial atoms. It is noted that C and N interstitials can give rise a significant MCA to Ni\(_2\)FeGa, while the effect of H interstitial is rather weaker. Following Table 2, it is clear that without interstitials (c/a=1.40), Fe atoms have the leading contribution to the MCA of 0.26 meV per atom, while the contribution from Ni (about -0.039 meV per atom) is an order of magnitude lower with opposite sign. The change in c/a from 1.35 to 1.40 has minor influence on the MCA and orbital moment. After considering interstitial N (H), the contribution for Ni-i atoms within the same plane is enhanced to 0.250 meV (0.097 meV) per atom. As to C interstitial atoms, the MCA of Ni-i atoms is slightly (Fig. 1(b)) increased to 0.039 meV per atom. That is, all types of the interstitial atoms lead to a significant change of the contribution to MCA for Ni-i. On the other hand, the orbital moments and thus the resulting MCA contribution are very comparable for the
Ni-ii atoms with and without interstitials, because the Ni-ii atoms are far away from the interstitials. Furthermore, for the H interstitial case, both the MCA and orbital moments of all Fe (including iii, iv and v) atoms change only slightly comparing to those in the pristine compound with imposed c/a=1.40, whereas the N and C interstitials lead to significant enhancement of contribution for Fe-iii atoms to MCA. For instance, the MCA contributions of Fe-iii atoms below the interstitials are increased to 0.681 meV and 0.508 meV per atom with N and C interstitials, more than two times larger that (0.260 meV) in the parent compound. Meanwhile the contributions from Fe-iv and Fe-v atoms are slightly reduced. Therefore, the interstitial atoms have very strong influence on the MCA of the local surrounding atoms, while the global tetragonal distortion has relatively marginal effects.

The effects of interstitials on MCAs and orbital magnetizations can be further understood based on the chemical bonding pairs between the interstitials and surrounding magnetic atoms. For instance, the octahedral center (interstitial) H, C and N to octahedral planar corner Ni-i almost have the same bond lengths as 1.85 Å, 1.88 Å and 1.88 Å. However, the integrated COHP of H-Ni bond is just -0.63 eV, which is much weaker than that of the comparable bond strength of C-(Ni-i) (-2.12 eV) and N-(Ni-i) (-1.96 eV) bonds. On the other hand, the octahedral below corner Fe-iii to the interstitial H, C and N have similar bond lengths as 1.65 Å, 1.83 Å and 1.83 Å, while the bond integrated COHP of H-Fe (iii) (-1.24 eV) can be comparable to that of C-(Fe-iii) (-2.88 eV) and N-(Fe-iii) (-2.38 eV) bonds. Obviously, the bond strengths of C interstitial to Fe-iii) and Ni-i are the strongest. This explains the significant change of orbital moments of Ni_2FeGa with C interstitial comparing to Ni_2FeGa at the same tetragonal distortion ratio without interstitial. In this view, the H interstitial just induce tetragonal distortion to Ni_2FeGa, while C and N interstitial not only induce tetragonal distortion but also change the chemical environment by forming strong bonds. We notice that the interstitial to planer Ni-i atom have comparable bond lengths as to lower Fe-iii atoms but weaker integrated COHP for each interstitial cases. Such bonding behaviors explains the effect of
interstitial on the magnetization and the MCA for Fe-iii atoms is stronger than that for Ni-i atoms.

4. Conclusion

Based on high-throughput DFT calculations, we investigated the effects of (H, B, C, and N) interstitials on the magnetic properties of cubic full Heusler compounds. We identified 32 compounds with substantial uniaxial MAE. Detailed analysis reveals that in addition to the breaking of the cubic symmetry, the changes in the local crystalline environment can induce significant contribution to the MAE, which can be attributed to the chemical bonding between the interstitial and surrounding magnetic atoms. This could provide an efficient way to design permanent magnets, which shall be explored further both experimentally and theoretically.

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Captions

**Figure captions:**

**Figure 1** (a) The possible interstitial sites in the convention Austenite unit cell of full Heusler compounds X\textsubscript{2}YZ. The blue and green octahedrons denote the 24f (0.25,0,0) and 24g (0.5,0.25,0.25) interstitial sites, while the red and pink tetrahedrons mark the 16e(0.125,0.875,0.875) and 16e(0.875,0.625,0.875) interstitial sites. (b) The crystal structure for the tetragonal full Heusler compound Ni\textsubscript{2}FeGa with interstitial (int.) at the most stable octahedral sites.

**Figure 2** Total energy as a function of tetragonal distortion ratio (c/a) for Fe\textsubscript{2}CoGa with and without interstitials. The reference energy is the energy of the compound in cubic inverse Heusler structure for Fe\textsubscript{2}CoGa with each interstitial as well as the parent compound. The opened and filled symbols represent the results Fe\textsubscript{2}CoGa in inverse and full Heusler structures, respectively. (b) The total energy as a function of tetragonal distortion ratio for Ni\textsubscript{2}FeGa in full Heusler structure with and without interstitials. Here the reference energy is the energy of the compound in cubic full Heusler structure.

**Table captions:**

**Table 1** The basic information of the most promising candidates of Heusler compounds with interstitials, where “site” marks the energetically preferred interstitial site, $\Delta H$ indicate the formation energy in unit of eV/atom, c/a ratio of resulting lattice constants along c-axis and in-plane, MAE in MJ/m\textsuperscript{3} and meV/f.u. (in parenthesis), total magnetic moment $M_{\text{tot}}$ in the unit of $\mu_B$/f.u., and the magnetization $M/V$ in the unit of $\mu_B$/Å\textsuperscript{3}. It should be noticed the general chemical formula for Heusler compound with interstitial is X\textsubscript{2}YZI\textsubscript{1/4}, where I is the interstitial.

**Table 2** The orbital moment ($\mu_l$, in unit of $\mu_B$) and the magneto-crystalline anisotropy energy (MCA, in unit of meV) energy values for Ni\textsubscript{2}FeGa with and without interstitials. Here the MCA is evaluated from Bruno’s formula. $\mu_l$ and $\sum$ (in unit of meV) denote the difference of orbital moment between two magnetization directions ([001] and [100]) and the summation of MCA energy, respectively. The general chemical formula for Heusler Ni\textsubscript{2}FeGa with interstitial is Ni\textsubscript{2}FeGaI\textsubscript{1/4}, where I is the interstitial.
Figures 1:

(a) [Diagram showing crystal structure with labels X, Y, Z, and atoms marked with colors such as int., Ni-i, Ni-ii, Fe-iii, Fe-iv, Fe-v, and Ga.]

(b) [Diagram showing a similar crystal structure with labels X, Y, Z, and atoms marked with the same colors.]

Figure 2:

(a) [Graph showing energy differences (E-E_{min}) as a function of c/a ratio with various curves representing different interactions (No int., B-int., N-int., H-int., C-int.).]

(b) [Graph showing a similar energy differences as a function of c/a ratio with curves for different interactions.]
Tables
| Parent | int. site | $\Delta H$ | c/a | $\text{MAE}$ | $M_{\text{tot}}$ | M/V |
|--------|---------|---------|-----|---------|---------|-----|
| Fe$_2$CoGa | B | 24f | -0.0616 | 1.45 | 1.4949 (0.4998) | 5.56 | 0.1120 |
|         | C | 24f | -0.0486 | 1.48 | 1.3017 (0.4072) | 5.37 | 0.1092 |
|         | N | 24f | -0.1088 | 1.50 | 1.3180 (0.4295) | 5.36 | 0.1089 |
|         | H | 24f | -0.0922 | 1.48 | 2.3677 (0.6863) | 5.95 | 0.1227 |
| Ni$_2$FeGa | C | 24f | -0.1207 | 1.40 | 0.9636 (0.2961) | 2.93 | 0.0595 |
|         | N | 24f | -0.1620 | 1.40 | 1.4292 (0.4386) | 2.97 | 0.0602 |
|         | H | 24f | -0.1916 | 1.39 | 0.5582 (0.1668) | 3.13 | 0.0654 |
| Fe$_2$CoGe | H | 24f | -0.0627 | 1.51 | 0.6291 (0.2080) | 5.48 | 0.1142 |
|         | N | 24f | -0.0576 | 1.56 | 0.4047 (0.1368) | 5.01 | 0.1025 |
| Fe$_2$NiAl | H | 24f | -0.2545 | 1.53 | 0.4947 (0.1298) | 4.56 | 0.0955 |
|         | N | 24f | -0.2842 | 1.57 | 0.5270 (0.1368) | 4.40 | 0.0902 |
| Fe$_2$NiGa | H | 24f | -0.1915 | 1.55 | 0.5670 (0.1298) | 4.67 | 0.0977 |
|         | B | 24f | -0.1219 | 1.51 | 0.7853 (0.1758) | 4.42 | 0.0893 |
|         | C | 24f | -0.1208 | 1.53 | 0.9217 (0.1863) | 4.31 | 0.0874 |
|         | N | 24f | -0.1620 | 1.53 | 1.3295 (0.2429) | 4.45 | 0.0939 |
| Co$_2$MnGa | C | 24f | -0.1289 | 1.13 | 0.5267 (0.6303) | 4.52 | 0.0920 |
|         | N | 24f | -0.1836 | 1.12 | 0.4755 (0.1576) | 4.76 | 0.0922 |
| Co$_2$MnGe | C | 24f | -0.0788 | 1.25 | 0.5388 (0.1226) | 4.06 | 0.0831 |
|         | N | 24f | -0.1226 | 1.29 | 0.5476 (0.1325) | 4.13 | 0.0841 |
| Co$_2$MnSi | C | 24f | -0.2571 | 1.21 | 0.5384 (0.1464) | 4.16 | 0.0898 |
| Rh$_2$MnAl | C | 24f | -0.5088 | 1.10 | 0.9501 (0.3336) | 4.25 | 0.0742 |
|         | N | 24f | -0.5457 | 1.06 | 1.1675 (0.4487) | 4.49 | 0.0784 |
| Rh$_2$NiSn | H | 24f | -0.2288 | 1.26 | 0.8236 (0.3063) | 0.99 | 0.0166 |
| Mn$_2$VGa | C | 24f | -0.1533 | 1.20 | 1.5038 (0.4874) | 2.26 | 0.0435 |
|         | B | 24f | -0.1474 | 1.23 | 1.8263 (0.5987) | 2.48 | 0.0472 |
|         | N | 24f | -0.2377 | 1.21 | 1.2674 (0.4087) | 2.34 | 0.0451 |
| Co$_2$FeAl | N | 24g | -0.2770 | 1.08 | 0.4881 (0.3009) | 5.01 | 0.1038 |
| Au$_2$MnAl | H | 16e | -0.1835 | 0.92 | 0.7732 (0.6489) | 3.82 | 0.0582 |
|         | N | 24g | -0.1975 | 1.27 | -0.4901 (-0.2412) | 3.66 | 0.0476 |
|         | C | 24g | -0.2770 | 1.21 | -0.5271 (-0.4923) | 3.82 | 0.0574 |
| Ni$_2$MnIn | C | 24f | -0.0057 | 1.21 | -1.0288 (-0.3513) | 3.96 | 0.0685 |
| Ni$_2$MnGa | H | 24f | -0.2519 | 1.27 | -1.3278 (-0.488) | 4.20 | 0.0852 |
|         | B | 24f | -0.2204 | 1.28 | -0.5822 (-0.185) | 4.02 | 0.0788 |
|         | C | 24f | -0.1780 | 1.29 | -0.9573 (-0.3031) | 3.91 | 0.0771 |
| Fe$_3$Ge | H | 24f | -0.0563 | 1.42 | 1.5018 (0.4655) | 6.44 | 0.1319 |
|         | B | 24f | -0.0254 | 1.16 | 0.5868 (0.1812) | 5.54 | 0.1211 |
| Fe$_3$Ga | B | 24f | -0.0710 | 1.21 | 0.6896 (0.2142) | 6.16 | 0.1229 |
|         | N | 24f | -0.1101 | 1.19 | 0.5184 (0.1610) | 5.92 | 0.1022 |
| Ni$_2$MnSn | B | 24g | -0.0959 | 1.06 | -0.6747 (-0.2064) | 3.75 | 0.0645 |
|         | C | 24g | -0.0480 | 1.17 | -0.4261 (-0.1421) | 3.70 | 0.0653 |
|         | N | 24g | -0.0892 | 1.17 | -0.4756 (-0.1613) | 3.74 | 0.0697 |
| Rh$_2$MnSn | C | 24f | -0.2679 | 1.28 | -0.8846 (-0.3529) | 3.66 | 0.0572 |
|                | Ni-i | Ni-ii | Fe-iii | Fe-iv | Fe-v | Σ    |
|----------------|------|-------|--------|-------|------|------|
| **H w/o int.** |      |       |        |       |      |      |
| [001]         | 0.024| 0.020 | 0.068  | 0.063 | 0.066| -    |
| [100]         | 0.019| 0.022 | 0.043  | 0.040 | 0.046| -    |
| Δ             | 0.005| -0.002| 0.025  | 0.023 | 0.020| -    |
| MCA           | 0.097| -0.039| 0.309  | 0.284 | 0.247| 0.330|
| **H w/ int.** |      |       |        |       |      |      |
| [001]         | 0.025| 0.020 | 0.068  | 0.067 | 0.072| -    |
| [100]         | 0.012| 0.024 | 0.013  | 0.053 | 0.049| -    |
| Δ             | 0.013| -0.004| 0.055  | 0.014 | 0.023| -    |
| MCA           | 0.250| -0.078| 0.681  | 0.173 | 0.285| 0.528|
| **C w/o int.**|      |       |        |       |      |      |
| [001]         | 0.013| 0.022 | 0.058  | 0.067 | 0.073| -    |
| [100]         | 0.011| 0.024 | 0.017  | 0.048 | 0.051| -    |
| Δ             | 0.002| -0.002| 0.041  | 0.019 | 0.021| -    |
| MCA           | 0.039| -0.039| 0.508  | 0.235 | 0.260| 0.316|
| **C w/ int.** |      |       |        |       |      |      |
| [001]         | 0.022| 0.065 |       | -     |      |      |
| [100]         | 0.024| 0.044 |       | -     |      |      |
| Δ             | -0.002| 0.021 |       | -     |      |      |
| MCA           | -0.039| 0.260 | 0.180  |      |      |      |

|                | c/a  | Ni    | Fe    | Σ    |
|----------------|------|-------|-------|------|
| **w/o int.**   |      |       |       |      |
| [001]         | 1.35 | 0.021 | 0.061 | -    |
| [100]         |      | 0.023 | 0.041 | -    |
| Δ             |      | -0.002| 0.020 | -    |
| MCA           |      | -0.039| 0.248 | 0.170|
| **w/ int.**   |      |       |       |      |
| [001]         | 1.40 | 0.021 | 0.061 | -    |
| [100]         |      | 0.023 | 0.041 | -    |
| Δ             |      | -0.002| 0.020 | -    |
| MCA           |      | -0.039| 0.248 | 0.170|
Highlights

- Rare earth free permanent magnets can be realized in tetragonally distorted full Heusler alloys induced by light interstitial atoms.
- Bain path calculations reveal that interstitials cause stable tetragonal distortion to full Heusler alloys.
- Analysis based on the perturbation theory and chemical bonding suggests that the uniaxial anisotropy can be attributed to change in the local crystalline environments around the interstitials.
- We postulate that this provides a universal way to tailor the magnetic properties of prospective permanent magnets.
Appendix A. Appendix
Table A.1: All the considered Heusler compounds (Com.) together with the ICSD ID number.

| Com.  | ID     | Com.  | ID     | Com.  | ID     | Com.  | ID     |
|-------|--------|-------|--------|-------|--------|-------|--------|
| Au₂MnAl | 57504  | Co₂CrAl | 57600  | Co₂FeAl | 57607  | Co₂HfAl | 110809 |
| Co₂MnAl | 606611 | Co₂NbAl | 57620  | Co₂TaAl | 606667 | Co₂TiAl | 606680 |
| Co₂VAI | 57643  | Co₂ZrAI | 57648  | Co₂CrGa | 102318 | Co₂CrIn | 416260 |
| Co₂FeGa | 102392 | Co₂FeGe | 247268 | Co₂FeIn | 102392 | Co₂FeSi | 622985 |
| Co₂HfGa | 102433 | Co₂MnGa | 623116 | Co₂NbGa | 623126 | Co₂TaGa | 102451 |
| Co₂TiGa | 102453 | Co₂VGa | 623228 | Co₂LiGe | 53673  | Co₂MnGe | 52971  |
| Co₂TiGe | 104969 | Co₂ZnGe | 52994  | Co₂HfSn | 102483 | Co₂MnSb | 53902  |
| Co₂MnSi | 106484 | Co₂MnSn | 102332 | Co₂NbSn | 102554 | Co₂ScSn | 102646 |
| Co₂TiSi | 53080  | Co₂VSi | 53086  | Co₂TiSn | 102583 | Co₂VSn | 102684 |
| Co₂ZrSn | 102687 | Cu₂CrAl | 57653  | Cu₂MnAl | 607012 | Cu₂CoSn | 103057 |
| Cu₂FeSn | 151205 | Cu₂MnIn | 102996 | Cu₂MnSb | 53312  | Cu₂MnSn | 103057 |
| Cu₂NiSn | 103069 | Fe₂CrAl | 184446 | Fe₂MnAl | 57806  | Fe₂MoAl | 57807  |
| Fe₂NiAl | 57808  | Fe₂TiAl | 57827  | Fe₂VAl | 57832  | Fe₂CoGa | 103473 |
| Fe₂CoGe | 52954  | Fe₂CrGa | 102755 | Fe₂NiGa | 103460 | Fe₂TiGa | 103469 |
| Fe₂VGa | 103473 | Fe₂MnSi | 632569 | Fe₂VSi | 53555  | Fe₂TiSn | 103641 |
| Fe₂VSn | 103644 | Mn₂VAl | 57994  | Mn₂RhGa | 247951 | Mn₂VGe | 103813 |
| Mn₂RuGe | 247950 | Mn₂RuSn | 247949 | Mn₂WSn | 104980 | Ni₂CrAl | 57662  |
| Ni₂HfAl | 57901  | Ni₂MnAl | 57976  | Ni₂NbAl | 58216  | Ni₂ScAl | 58050  |
| Ni₂TaAl | 58055  | Ni₂TiAl | 58063  | Ni₂VAl | 58071  | Ni₂ZrAl | 58081  |
| Ni₂CuSb | 53320  | Ni₂CuSn | 103068 | Ni₂HfGa | 103734 | Ni₂MnGa | 103803 |
| Ni₂NbGa | 103839 | Ni₂ScGa | 103874 | Ni₂TaGa | 103881 | Ni₂TiGa | 103886 |
| Ni₂VGa | 103892 | Ni₂ZrGa | 103902 | Ni₂LiGe | 53673  | Ni₂MnGe | 192566 |
| Ni₂ZrGe | 53865  | Ni₂HfIn | 54595  | Ni₂HfSn | 104250 | Ni₂MgIn | 51982  |
| Ni₂MnIn | 639954 | Ni₂ScIn | 59446  | Ni₂TiIn | 59451  | Ni₂ZrIn | 59460  |
| Ni₂LiSi | 44819  | Ni₂LiSn | 25325  | Ni₂MgSb | 104841 | Ni₂MgSn | 104842 |
| Ni₂TiSb | 76700  | Ni₂ZrSb | 76703  | Ni₂ScSn | 105339 | Ni₂TiSn | 105369 |
| Ni₂VSn | 105376 | Ni₂ZrSn | 105383 | Pd₂MnAl | 57981  | Pd₂MnAs | 107955 |
| Ni₂NbSn | 105181 | Pd₂MnGe | 53705  | Rh₂NiSn | 105327 | Pd₂MnIn | 51990  |
| Pd₂MnSb | 643312 | Pd₂MnSn | 104945 | Rh₂MnAl | 57986  | Rh₂MnGe | 53706  |
| Rh₂MnPb | 104936 | Rh₂MnSn | 104964 | Ru₂FeSi | 53525  | Ru₂FeSn | 103615 |
| Fe₂Al | 57793  | Fe₂Ga | 108436 | Fe₂Ge | 53462  | Fe₂Si | 53545  |
| Mn₂Si | 76227  | Ni₃Al | 58038  | Ni₃Sb | 76693  | Ni₃Sn | 105354 |
