Large magnetocrystalline anisotropy in tetragonally distorted Heuslers: a systematic study

To cite this article: Y-I Matsushita et al 2017 J. Phys. D: Appl. Phys. 50 095002

View the article online for updates and enhancements.

Related content
- From soft to hard magnetic Fe–Co–B by spontaneous strain: a combined first principles and thin film study
- Mn2Ga-based Heusler alloys with low net moment and high spin polarization
- A scheme for spin-selective electron localization in Mn3Ga Heusler material

Recent citations
- Ab-initio study of X-Ray Absorption and X-Ray Magnetic Circular Dichroism Spectra of Mn2PtGa and Co2PtGa alloys

IOP ebooks
Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.
Start exploring the collection - download the first chapter of every title for free.
Large magnetocrystalline anisotropy in tetragonally distorted Heuslers: a systematic study

Y-I Matsushita1,2,7, G Madjarova1,3, J K Dewhurst1, S Shallcross4, C Felser5, S Sharma1,6,7 and E K U Gross1

1 Max-Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany
2 Department of Applied Physics, The University of Tokyo, Tokyo 113-8656, Japan
3 Department of Physical Chemistry, Faculty of Chemistry and Pharmacy, Sofia University, 1126 Sofia, Bulgaria
4 Lehrstuhl für Theoretische Festkörperphysik, Staudtstr. 7-B2, 91058 Erlangen, Germany
5 Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Strasse 40, 01187 Dresden, Germany
6 Department of Physics, Indian Institute of Technology, Roorkee, 247667 Uttarkhand, India

E-mail: sharma@mpi-halle.mpg.de and matsushita@ap.t.u-tokyo.ac.jp

Received 23 October 2016, revised 12 December 2016
Accepted for publication 16 December 2016
Published 1 February 2017

Abstract

With a view to the design of hard magnets without rare earths we explore the possibility of large magnetocrystalline anisotropy energies in Heusler compounds that are unstable with respect to a tetragonal distortion. We consider the Heusler compounds Fe2YZ with Y = (Ni, Co, Pt), and Co2YZ with Y = (Ni, Fe, Pt) where, in both cases, Z = (Al, Ga, Ge, In, Sn). We find that for the Co2NiZ, Co2PtZ, and Fe2PtZ families the cubic phase is always, at T = 0, unstable with respect to a tetragonal distortion, while, in contrast, for the Fe2NiZ and Fe2CoZ families this is the case for only 2 compounds—Fe2NiGe and Fe2NiSn. For all compounds in which a tetragonal distortion occurs we calculate the magnetocrystalline anisotropy energy (MAE) finding remarkably large values for the Pt containing Heuslers, but also large values for a number of the other compounds (e.g. Co2NiGa has an MAE of $-2.38 \text{ MJ m}^{-3}$). The tendency to a tetragonal distortion we find to be strongly correlated with a high density of states (DOS) at the Fermi level in the cubic phase. As a corollary to this fact we observe that upon doping compounds for which the cubic structure is stable such that the Fermi level enters a region of high DOS, a tetragonal distortion is induced and a correspondingly large value of the MAE is then observed.

Keywords: Heusler compounds, tetragonal distortion, ab initio calculations

(Some figures may appear in colour only in the online journal)
values. However, as the rare earths are both costly and highly polluting to extract from ore there is a current focus on the design of hard magnets without rare earths [2–5]. Magnetic materials having a low crystal symmetry evidently possess a natural spatial anisotropy, and this in turn can lead to very large values of the MAE. Such low symmetry magnets therefore offer a promising design route towards the next generation of hard magnets. Accurate calculation of the MAE requires sophisticated and computationally expensive first principles calculations, making difficult the kind of high throughput search that might be expected to yield interesting high MAE materials. In this paper we show that for a promising materials class— the Heusler alloys—the density of the states at the Fermi level provides a very good indicator of the propensity to distortion, and therefore of the likelihood of finding a high MAE material within this class. The use of such material markers for high MAE can, we believe, significantly alleviate the computation bottleneck preventing high throughput search.

The Heusler materials have attracted sustained attention due both to their exceptional magnetic properties as well as a huge variety of possible compounds that may be experimentally realized [6, 7]; reviews may be found in [8–11]. These materials, which consist of 4 inter-penetrating face centred cubic lattices, often exhibit a symmetry lowering structural transition to a tetragonal or hexagonal phase [1, 12–15], raising the possibility of a crystal symmetry lowering induced large MAE. For Mn rich Heusler alloys this has previously been explored [13, 16]; here we consider this possibility in the Heusler family of Fe2YZ with Y = (Ni, Co, Pt), and Co2YZ with Y = (Ni, Fe, Pt) where, in both cases, Z = (Al, Ga, Ge, In, Sn).

Our principle findings are that (i) the Co2NiZ and Co2PtZ classes naturally distort to a tetragonal structure with clathrate values in the range 1.3–1.5; (ii) the Fe rich Heuslers generally do not distort, with the exceptions of Fe2NiZ where Z = Ge or Sn and the Fe2PtZ family; (iii) this distortion can induce a very high MAE—of up to 5 MJ m–3 for the Pt containing Heuslers, comparable to the best known transition metal magnet L10-FePt, and of up to 1 MJ m–3 for the Co rich but Pt free Heuslers. In each case where a distortion occurs the volume change is found to be very small (a few percent at most), with the exception of Fe2PtGe in which a 6% increase of volume occurs upon distortion.

We furthermore find that this tendency to tetragonal distortion strongly correlates to a rather simple material descriptor, namely the density of states (DOS) at the Fermi level. A high DOS favours tetragonal distortion and, on this basis, we consider the possibility of inducing a tetragonal distortion by moderate doping (via a virtual crystal approximation) that shifts the Fermi energy from a low to a high DOS position. Consistent with the validity of this material descriptor we find that the Heusler alloys Co2FeAl and Co2FeSn—in which the Fermi energy lies far from and close to a high DOS region respectively—all spontaneously suffer tetragonal distortion upon doping.

### 2. Calculation details

For structural relaxation we use the Vienna ab initio simulation package (VASP) [17] with projector augmented wave (PAW) pseudopotentials [18], a plane-wave-basis set energy cutoff of 400 eV, and the Perdew–Burke–Ernzerhof (PBE) functional [19]. Reciprocal space integration has been performed with a Γ-centered Monkhorst–Pack 10 × 10 × 10 mesh. The structural optimization has been converged to a tolerance of 10−5 eV, whereas the MAE values were obtained with a tolerance of 10−7 eV. All calculations are performed in the presence of spin–orbit coupling term. For the calculation of the MAE we have also deployed the all-electron full-potential linearized augmented-plane wave (FP-LAPW) code Elk [20]. The definition of MAE adopted in this study is the following:

\[
\text{MAE} = E_{\{100\}}^{\text{tot}} - E_{\{001\}}^{\text{tot}}
\]

where \(E_{\{100\}}^{\text{tot}}(E_{\{001\}}^{\text{tot}})\) represents the total energy with spin orientation in the [100] ([001]) direction. A positive value of the MAE therefore indicates that out-of-plane spin configuration is energetically favourable, whereas a negative one that the in-plane direction is favourable.

The Heusler structure is described by the X2YZ general formula, in which the species X and Y are transition metal elements whereas the Z atom is p-orbital element with metal character (from III or IV main groups). The crystal structure consists of four inter-penetrating face centred cubic lattices and belongs to the 225 (Fm-3m) symmetry group for the regular Heusler structure, and 216 (F-43m) for the inverse Heuslers; Wyckoff positions of the atoms are presented in table 1.

### 3. Structural distortion

We first consider the stability with respect to tetragonal distortion of the Heusler alloys X2YZ in which the X sub-lattices are occupied by either Fe or Co, the Y sub-lattice by Fe, Co, Ni, or Pt, and Z sub-lattice by Al, Ge, Ga, Sn, or In. This represents 30 materials in total, of which 10 have been previously experimentally synthesized; for details we refer the reader to tables A1 and A2 of appendix. In figure 1 we present the DOS at the Fermi energy of each of these Heusler materials for both the high symmetry cubic phase and, where it exists, the tetragonal structure. For the Co rich Heuslers Co2NiZ and Co2PtZ the high symmetry phase is always unstable with respect to tetragonal distortion while, in contrast, in the case of the Fe containing Heuslers the cubic phase is generally stable. There are two exceptions to this latter rule: Fe2NiGe and Fe2NiSn, and the Fe2PtZ family. For all cases where the tetragonal phase is stable we find the clathrate ratios in the range 1.3–1.5 with the high end clathrate ratios found for the Fe2YZ Heuslers in which Z is either Ge or Sn (curiously, as we will see, these are also the Heusler compounds that have

| Table 1. Structural order of regular and inverse Heusler structures. |
|-----------------------|---------------------|---------------------|---------------------|
| 4a        | 4c                   | 4b                   | 4d                   |
| (0,0,0)   | (1/4,1/4,1/4)        | (1/2,1/2,1/2)        | (3/4,3/4,3/4)        |
| Regular   | Z                    | X                    | Y                    | X                    |
| Inverse   | Z                    | Y                    | X                    | X                    |

Y-I Matsushita et al.
the desired positive MAE). Of the Heuslers in figure 1 that have been experimentally synthesized only one, Co₂NiGa, is observed in the tetragonal structure, in agreement with our calculations; all others are found to be cubic, also in agreement with our calculations (with the exception of Fe₂NiGe for which we predict a tetragonal structure, this case will be discussed in detail below).

For each structure we have also determined whether the material takes on a regular or inverse occupation of the sublattices. As may be seen in figure 1 most of the structures are inverse Heusler except for the Co₂FeZ family where the regular cubic structure has a lower ground state energy. This finding is in a good agreement with an empirical rule first stated in [10]: when the electronegativity of the Y element is larger than that of the X element the system prefers the inverse Heusler structure, with otherwise the regular Heusler structure realized. There are, however, two deviations from this rule in our results. We find that Fe₂NiGe and Fe₂NiSn adopt a tetragonally distorted regular structure, in agreement with previous theoretical work [21], but in contrast to the inverse structure expected on the basis of the empirical rule (the electronegativity of Ni is higher than that of Fe).

In [22] experiment reports, in agreement with the semi-empirical rule, a cubic inverse structure for Fe₂NiGe. Accompanying theoretical calculations [22], however, find that the energy change due to antisite disorder is always much smaller than the thermal energy available due to annealing (which takes place at 650 K in the experiment). The authors of [22] therefore conclude that annealing will control the state of order for the Fe₂NiZ family. The mismatch between experiment and our results, calculated for fully ordered structures, therefore likely has its origin in thermal induced substitutional disorder. It is worth pointing out that the energy difference between the tetragonally distorted regular structure (our lowest energy structure) and the inverse cubic structure is 120 meV, i.e. about double the thermal energy due to annealing. This indicates that the presence of antisite disorder has a significant impact on the propensity of this material towards tetragonal disorder and that, at least for the Fe₂NiZ family, the coupling between disorder and tetragonal distortion is a subject worthy of further investigation.

We now consider the electronic origin of the instability of the cubic phase with respect to a tetragonal distortion. Such instability of the high symmetry phase has been observed in many Heusler compounds, in particular the Mn rich Heuslers [13, 16, 23], and has been attributed to a number of different mechanisms: a Jahn–Teller effect [23], a ‘band’ JT effect [24], a nesting induced Fermi surface instability [25], and anomalous phonon modes [26, 27].

In figure 2 we present the total density of states for four representative examples of the set of Heusler compounds we investigate. For all four cases (and for all Heuslers we study in this work) the minority spin channel is not significantly involved in the mechanism of distortion, having a very low DOS near the Fermi energy. For the cases (Co₂NiAl, Fe₂NiGe) in which the cubic phase is unstable we see a clear redistribution of spectral weight near the Fermi energy, such that a high DOS near $E_F$ is lowered by the opening up of a ‘valley’ near $E_F$ in the tetragonal phase. On the other hand, for the materials in
which the cubic phase is stable the DOS at $E_F$ is already very low (see the right hand panels of figure 2 for the representative cases of Co$_2$FeAl and Fe$_2$CoGe). As may be seen in figure 3 for the case of Co$_2$NiAl this redistribution of weight occurs in all species and momentum channels, but with states of Co character being the more important. Interestingly, it is seen that the redistribution occurs particularly in states of $e_g$ character.

4. Magnetic moments and magnetocrystalline anisotropy

In figure 4 we present the total magnetic moment, saturation magnetization $M_s$ and MAE for the Co$_2$YZ and Fe$_2$YZ Heusler families. In all systems the magnetic order is found to be ferromagnetic. To a good approximation the values of the saturation magnetization $M_s$ fall into four distinct bands: (i) $M_s$ close to 500 kA m$^{-1}$ for Co$_2$NiZ; (ii) $M_s$ close to 900 kA m$^{-1}$ for Co$_2$FeZ, Fe$_2$NiZ, and Fe$_2$CoZ; (iii) $M_s$ close to 450 kA m$^{-1}$ for Co$_2$PtZ; and (iv) $M_s$ close to 800 kA m$^{-1}$ for Fe$_2$PtZ. From the viewpoint of hard magnetic applications a high value of the saturation magnetization is desired, and from this point of view the Co$_2$FeZ, Fe$_2$NiZ, Fe$_2$CoZ, and Fe$_2$PtZ compounds are most interesting. For comparison we recall that the two ‘standard’ hard magnets have saturation magnetizations of 970 kA m$^{-1}$ for SmCo$_5$ and 1280 kA m$^{-1}$ for Nd$_2$Fe$_14$B.

We now turn to a discussion of the MAE values realized in the cases for which a tetragonal distortion occurs (see also figure 4). We first note that a positive value of the MAE indicates that the magnetic moments all align with the symmetry axis of the tetragonally distorted material: this is essential for hard magnetic applications. When the MAE takes on a negative value this indicates that the moments are in the plane perpendicular to this symmetry axis. We have checked the energy required to rotate spins in-plane finding, as expected, a very soft energy dependence. This freedom to rotate the spin structure obviously renders such cases entirely unsuitable for hard magnetic application. We will therefore focus on those cases for which the MAE is positive.
Of the 15 compounds that suffer a tetragonal distortion only 6 have $E_{\text{MAE}}>0$. Curiously, these are the compounds for which the Z element is either Ge or Sn: Co$_2$NiGe, Fe$_2$NiGe, Fe$_2$NiSn, Co$_2$PtSn, Fe$_2$PtGe, and Fe$_2$PtSn. The values of the MAE for the Pt free compounds are all, as expected, modest as compared to the Pt containing compounds. The maximum positive MAE for Pt free compounds are found in Fe$_2$NiGe and Fe$_2$NiSn, with an MAE of $1 \approx 5.19$ MJ m$^{-3}$, while for the Pt containing compounds we find a much higher MAE of 5.19 MJ m$^{-3}$ for Fe$_2$PtGe. This value is close to the currently highest value observed for an MAE in a rare earth free material (a value of 7 MJ m$^{-3}$ for L$_{10}$-FePt [28]). The rather high $M_s$ value of 516 kA m$^{-1}$ suggests this material might be interesting to further explore in the context of specialist application as a hard magnet.

5. Distortion control

The previous two sections lead us to conclude that (i) the propensity to tetragonal distortion strongly correlates with a high DOS at the Fermi energy in the cubic phase and (ii) that if a tetragonal distortion occurs, high values of the MAE are possible. This raises the possibility of, with a view to engineering a high MAE, inducing such a distortion by doping.

To this end we consider the two materials presented in figure 2 in which the Fermi energy lies in the valley between the two high DOS regions, and dope the cubic phase within the virtual crystal approximation (VCA). In the case of Co$_2$FeAl a doping of 1.5 electrons is required to shift the Fermi energy into the high DOS region, with a more modest 0.3 electrons required in the case of Co$_2$FeSn. In both cases we find that upon such doping, the cubic phase becomes unstable with respect to a tetragonal distortion; structural details may be found in table 2. A subsequent calculation of the MAE finds values comparable to those obtained for the naturally tetragonally distorting Heusler compounds. It is also interesting to note that the mechanism of the distortion appears to be somewhat different from the ‘natural’ cases: while in figure 2 it is clearly seen that the distortion results in a significant redistribution of spectral weight away from the Fermi energy via the opening of a ‘repulsion valley’ in figure 5 this effect is seen to be much weaker. This of course, may be an artifact of the VCA.

Of the 15 compounds that suffer a tetragonal distortion only 6 have $E_{\text{MAE}}>0$. Curiously, these are the compounds for which the Z element is either Ge or Sn: Co$_2$NiGe, Fe$_2$NiGe, Fe$_2$NiSn, Co$_2$PtSn, Fe$_2$PtGe, and Fe$_2$PtSn. The values of the MAE for the Pt free compounds are all, as expected, modest as compared to the Pt containing compounds. The maximum positive MAE for Pt free compounds are found in Fe$_2$NiGe and Fe$_2$NiSn, with an MAE of $\approx 1$ MJ m$^{-3}$, while for the Pt containing compounds we find a much higher MAE of 5.19 MJ m$^{-3}$ for Fe$_2$PtGe. This value is close to the currently highest value observed for an MAE in a rare earth free material (a value of 7 MJ m$^{-3}$ for L$_{10}$-FePt [28]). The rather high $M_s$ value of 516 kA m$^{-1}$ suggests this material might be interesting to further explore in the context of specialist application as a hard magnet.

5. Distortion control

The previous two sections lead us to conclude that (i) the propensity to tetragonal distortion strongly correlates with a high DOS at the Fermi energy in the cubic phase and (ii) that if a tetragonal distortion occurs, high values of the MAE are possible. This raises the possibility of, with a view to engineering a high MAE, inducing such a distortion by doping.

To this end we consider the two materials presented in figure 2 in which the Fermi energy lies in the valley between the two high DOS regions, and dope the cubic phase within the virtual crystal approximation (VCA). In the case of Co$_2$FeAl a doping of 1.5 electrons is required to shift the Fermi energy into the high DOS region, with a more modest 0.3 electrons required in the case of Co$_2$FeSn. In both cases we find that upon such doping, the cubic phase becomes unstable with respect to a tetragonal distortion; structural details may be found in table 2. A subsequent calculation of the MAE finds values comparable to those obtained for the naturally tetragonally distorting Heusler compounds. It is also interesting to note that the mechanism of the distortion appears to be somewhat different from the ‘natural’ cases: while in figure 2 it is clearly seen that the distortion results in a significant redistribution of spectral weight away from the Fermi energy via the opening of a ‘repulsion valley’ in figure 5 this effect is seen to be much weaker. This of course, may be an artifact of the VCA.

Table 2. Calculated material properties of Co$_2$FeAl, Co$_2$FeSn, and their electron doped systems. The most stable structure is shown in the 2nd column. The calculated magnetic moments per formula unit, lattice parameters, $a$ and $c$, and the magnetocrystalline anisotropy energies for the tetragonal cases are also listed.

| Structure                | $\mu_B^{\text{tot}}$ | $a_{\text{calc}}, c_{\text{calc}}$ (Å) | MAE (MJ m$^{-3}$) |
|--------------------------|----------------------|----------------------------------------|-------------------|
| Co$_2$FeAl               | Regular cubic        | 5.08                                   | --                |
| 1.5e$^-$ doped-Co$_2$FeAl| Regular tetragonal   | 5.43                                   | $a = c = 6.16$ $e = 6.88$ $-0.94$ |
| Co$_2$FeSn               | Regular cubic        | 5.66                                   | --                |
| 0.3e$^-$ doped-Co$_2$FeAl| Regular tetragonal   | 5.41                                   | $a = 5.97$ $c = 6.45$ $-1.30$ |

Figure 4. Magnetic moments and MAE for the Heusler compounds Co$_2$NiZ, Co$_2$FeZ, Fe$_2$NiZ, and Fe$_2$CoZ where Z = Al, Ge, Ga, Sn, or In. Values of the MAE are presented only for tetragonally distorted Heusler compounds; the MAE for the cubic phase is, in comparison, negligibly small. A positive value of the MAE indicates an out-of-plane easy axis (i.e. the moments are aligned with the distortion axis), while a negative value an in-plane easy axis (i.e. the moments lie within the plane perpendicular to the distortion direction). For comparison, the value of MAE for Nd$_2$Fe$_4$B is 4.4 (MJ m$^{-3}$), and saturation magnetization is 1280 (kA m$^{-1}$).

| Structure | $\mu_B^{\text{tot}}$ | $a_{\text{calc}}, c_{\text{calc}}$ (Å) | MAE (MJ m$^{-3}$) |
|-----------|----------------------|----------------------------------------|-------------------|
| Co$_2$FeAl | Regular cubic        | 5.08                                   | --                |
| 1.5e$^-$ doped-Co$_2$FeAl | Regular tetragonal   | 5.43                                   | $a = c = 6.16$ $e = 6.88$ $-0.94$ |
| Co$_2$FeSn | Regular cubic        | 5.66                                   | --                |
| 0.3e$^-$ doped-Co$_2$FeAl | Regular tetragonal   | 5.41                                   | $a = 5.97$ $c = 6.45$ $-1.30$ |
6. Conclusion

We have addressed the question of whether we may obtain large magnetocrystalline anisotropy energies in Heusler compounds that adopt a low symmetry tetragonal structure. To this end we have investigated the Heusler compounds Fe$_2$YZ with Y = (Ni, Co, Pt), and Co$_2$YZ with Y = (Ni, Fe, Pt) where, in both cases, Z = (Al, Ga, Ge, In, Sn). We find that the cubic phase of 15 of these 30 Heusler compounds is unstable with respect to tetragonal distortion, in particular for the Co$_2$PtZ, Co$_2$NiZ, and Fe$_2$PtZ families the cubic phase is always, at $T=0$, unstable. In contrast, for the Fe$_2$NiZ and Fe$_2$CoZ families this is the case for only 2 compounds—Fe$_2$NiGe and Fe$_2$NiSn. The mechanism behind this distortion involves a significant redistribution of spectral weight near the Fermi energy, such that a ‘valley’ in the DOS at the Fermi energy is opened up in the tetragonal phase leading to a reduction in the number of states near the Fermi energy. Curiously, we find that for the compounds we investigate a good rule of thumb exists that if the DOS at the Fermi level is greater than 4.5 states eV$^{-1}$, the cubic phase is unstable.

Of the 15 compounds that suffer tetragonal distortion the magnetocrystalline anisotropy energies are found to range in values from $-12$ MJ m$^{-3}$ (Co$_2$PtAl) to $+5.19$ MJ m$^{-3}$ (Fe$_2$PtGe). As expected, the values of the MAE for the Pt free Heuslers are more modest in magnitude, and range in value from $-2.38$ MJ m$^{-3}$ (Co$_2$NiGa) to 1.09 MJ m$^{-3}$ (Fe$_2$NiSn).

For hard magnet application only positive values of the magnetocrystalline anisotropy energies, which correspond to moments aligned with the tetragonal symmetry axis, are interesting. Interestingly, we find that the MAE takes on a positive value for all cases in which the Z element is either Ge or Sn.

Finally, we have considered the possibility of doping the Heusler compounds in which the cubic phase is stable in order to induce a tetragonal distortion. Using the virtual crystal approximation we find that this is indeed possible, and the doping induced distortion results in magnetocrystalline anisotropy energies values comparable to those obtained in the naturally distorting Heusler compounds.

Acknowledgments

YM, GM and S Sharma would like to thank the Heusler project funded by the MPG.

Appendix. Details of the structural and magnetic properties of the Heuslers investigated in this work

In this appendix we present structural details of the Heusler compounds calculated in the manuscript along with experimental structure data where this exists. In table A1 we present the Heusler compounds Co$_2$NiZ, Co$_2$FeZ, and in table A2 the compounds Fe$_2$NiZ, and Fe$_2$CoZ where in each case Z = Al, Ge, Ga, Sn, or In.
Table A1. Calculated material properties of Co-family Heusler materials in cubic and tetragonal structures. The most stable structure in regular Heusler (denoted by ‘reg.’) and inverse Heusler (denoted by ‘inv.’) with cubic or tetragonal (denoted by ‘tet.’) symmetry are shown in the 2nd column. The calculated total energy and magnetic moments per formula unit, distortion parameter \( c/a \), saturated magnetic moment \( M_s \), atom resolved moments, and MAE values are also listed. Note that two X atoms are not equivalent in inverse Heusler with cubic or tetragonal symmetry. Therefore, two values of atom resolved moments for X elements are listed in inverse Heusler materials.

| Structure  | Moment(\(\mu_0\)) | \(a_{\text{calc}}, c_{\text{calc}}\) (Å) | \(M_s\) (kA m\(^{-1}\)) | MAE (MJ m\(^{-3}\)) | expt. |
|------------|------------------|-------------------|-----------------|-----------------|-------|
| CoNiAl inv. tet. | 2.78 (Co = 1.4, 1.2 Ni = 0.2) | \(a = 5.20, c = 6.76\) | 564 | -2.11 |
| CoNiGa inv. tet. | 2.79 (Co = 1.6, 1.4 Ni = 0.2) | \(a = 5.19, c = 6.80\) | 562 | -2.38 |
| CoNiGe inv. tet. | 2.46 (Co = 1.3, 1.0 Ni = 0.2) | \(a = 5.12, c = 6.97\) | 498 | 0.86 |
| CoNiIn inv. tet. | 2.49 (Co = 1.6, 1.3 Ni = 0.2) | \(a = 5.43, c = 7.13\) | 527 | -2.22 |
| CoNiSn inv. tet. | 2.58 (Co = 1.4, 1.1 Ni = 0.2) | \(a = 5.37, c = 7.22\) | 458 | 0 |
| CoFeAl reg. cubic | 5.08 (Co = 1.2, 1.2 Fe = 2.8) | \(a = c = 5.69\) | 1016 | — |
| CoFeGa reg. cubic | 5.07 (Co = 1.2, 1.2 Fe = 2.8) | \(a = c = 5.70\) | 1005 | — |
| CoFeGe reg. cubic | 5.60 (Co = 1.4, 1.4 Fe = 2.9) | \(a = c = 5.74\) | 1099 | — |
| CoFeIn reg. cubic | 5.23 (Co = 1.3, 1.3 Fe = 2.8) | \(a = c = 5.64\) | 908 | — |
| CoFeSn reg. cubic | 5.66 (Co = 1.4, 1.4 Fe = 2.9) | \(a = c = 5.64\) | 974 | — |
| CoPtAl inv. tet. | 2.84 (Co = 1.5, 1.2 Pt = 0.1) | \(a = 5.36, c = 7.13\) | 516 | -12 |
| CoPtGa inv. tet. | 2.88 (Co = 1.6, 1.3 Pt = 0.1) | \(a = 5.36, c = 7.21\) | 516 | -11.33 |
| CoPtGe inv. tet. | 2.52 (Co = 1.5, 1.0 Pt = 0.1) | \(a = 5.32, c = 7.31\) | 453 | -1.01 |
| CoPtIn inv. tet. | 3.08 (Co = 1.6, 1.4 Pt = 0.1) | \(a = 5.50, c = 7.67\) | 493 | -6.94 |
| CoPtSn inv. tet. | 2.59 (Co = 1.5, 1.1 Pt = 0.1) | \(a = 5.50, c = 7.63\) | 416 | 0.42 |

Table A2. Calculated material properties of Fe-family Heusler materials in cubic and tetragonal structures. The most stable structure in regular Heusler (denoted by ‘reg.’) and inverse Heusler (denoted by ‘inv.’) with cubic or tetragonal (denoted by ‘tet.’) symmetry are shown in the 2nd column. The calculated total energy and magnetic moments per formula unit, distortion parameter \( c/a \), saturated magnetic moment \( M_s \), atom resolved moments, and MAE values are also listed. Note that two X atoms are not equivalent in inverse Heusler with cubic or tetragonal symmetry. Therefore, two values of atom resolved moments for X elements are listed in inverse Heusler materials.

| Structure  | Moment(\(\mu_0\)) | \(a_{\text{calc}}, c_{\text{calc}}\) (Å) | \(M_s\) (kA m\(^{-1}\)) | MAE (MJ m\(^{-3}\)) | expt. |
|------------|------------------|-------------------|-----------------|-----------------|-------|
| FeNiAl inv. cubic | 4.86 (Fe = 2.6, 1.8 Ni = 0.5) | \(a = c = 5.74\) | 954 | — |
| FeNiGa inv. cubic | 4.91 (Fe = 2.6, 1.9 Ni = 0.4) | \(a = c = 5.77\) | 955 | — |
| FeNiGe reg. tet. | 4.86 (Fe = 2.3, 2.3 Ni = 0.3) | \(a = 5.02, c = 7.59\) | 944 | 1.07 |
| FeNiIn inv. cubic | 5.22 (Fe = 2.7, 2.2 Ni = 0.4) | \(a = c = 6.07\) | 885 | — |
| FeNiSn reg. tet. | 5.02 (Fe = 2.4, 2.4 Ni = 0.3) | \(a = 5.22, c = 8.02\) | 853 | 1.09 |
| FeCoAl inv. cubic | 5.14 (Fe = 2.5, 1.6 Co = 1.0) | \(a = c = 5.71\) | 1026 | — |
| FeCoGa inv. cubic | 5.28 (Fe = 2.5, 1.8 Co = 1.1) | \(a = c = 5.76\) | 1041 | — |
| FeCoGe inv. cubic | 5.13 (Fe = 2.7, 1.5 Co = 1.0) | \(a = c = 5.72\) | 1019 | — |
| FeCoIn inv. cubic | 6.18 (Fe = 2.7, 2.3 Co = 1.3) | \(a = c = 6.03\) | 1053 | — |
| FeCoSn inv. cubic | 5.54 (Fe = 2.7, 1.9 Co = 1.1) | \(a = c = 5.99\) | 959 | — |
| FePtAl inv. cubic | 5.04 (Fe = 2.8, 2.1 Pt = 0.2) | \(a = c = 5.97\) | 885 | — |
| FePtGa inv. tet. | 5.06 (Fe = 2.7, 2.3 Pt = 0.2) | \(a = 5.50, c = 7.10\) | 873 | -5.41 |
| FePtGe reg. tet. | 5.27 (Fe = 2.6, 2.6 Pt = 0.1) | \(a = 5.40, c = 7.38\) | 893 | 5.19 |
| FePtIn inv. tet. | 5.27 (Fe = 2.8, 2.5 Pt = 0.1) | \(a = 5.64, c = 7.56\) | 812 | -3.57 |
| FePtSn reg. tet. | 5.26 (Fe = 2.6, 2.6 Pt = 0.1) | \(a = 5.64, c = 7.58\) | 802 | 2.97 |

References

[1] Winterlik J et al 2012 Adv. Mater. 24 6283
[2] McCallum R W, Lewis L H, Skomrski R, Kramer M J and Anderson I E 2014 Annu. Rev. Mater. Res. 44 451
[3] Coey J M D 2011 IEEE Trans. Magn. 47 4671
[4] Coey J M D 2012 Scr. Mater. 67 524
[5] Kramer M J, McCallum R W, Anderson I A and Constantinides S 2012 JOM 64 752
[6] Lue C S and Kuo Y K 2002 Phys. Rev. B 66 085121
[7] Alijani V et al 2011 Phys. Rev. B 84 224416
[8] Felser C, Fecher G H and Balke B 2007 Angew. Chem., Int. Ed. 46 668
[9] Graf T, Felser C and Parkin S S P 2011 Prog. Solid State Chem. 39 1
[10] Graf T, Winterlik J, Muchler L, Fecher G H, Felser C and Parkin S S 2013 Handbook Magn. Mater. 21 1
[11] Kreiner G, Kalache A, Hausdorf S, Alijani V, Qian J-F, Burkhardt U, Ouardi S and Felser C 2014 Z. Anorg. Allg. Chem. 640 738
[12] Roy T and Chakrabarti A 2017 J. Mag. Magn. Mater. 423 395
[13] Wollmann L, Chadov S, Kübler J and Felser C 2015 Phys. Rev. B 92 064417
[14] Talapatra A, Arróyave R, Entel P, Valencia-Jaime I and Romero A H 2015 Phys. Rev. B 92 054107
[15] Hongzhi L, Pengzhong J, Guodong L, Fanbin M, Heyan L, Enke L, Wenhong W and Guangheng W 2013 Solid State Commun. 170 44–7
[16] Wollmann L, Chadow S, Kübler J and Felser C 2014 Phys. Rev. B 90 214420
[17] Kresse G and Furthmüller J 1996 Comput. Mater. Sci. 6 15
[18] Blöchl P 1994 Phys. Rev. B 50 17953
[19] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[20] Dewhurst J K et al 2016 http://elk.sourceforge.net/
[21] Gillessen M and Dronskowski R 2010 J. Comput. Chem. 31 612
[22] Gasi T et al 2013 Phys. Rev. B 87 064411
[23] Felser C and Hirohata A E 2016 Heusler Alloys Springer Series in Materials Science p 222 (www.springer.com/gp/book/9783319214481)
[24] Suits J 1976 Solid State Commun. 18 423
[25] Barman S R, Banik S, Shukla A K, Kamal C and Chakrabarti A 2007 Europhys. Lett. 80 57002
[26] Zayak A T, Entel P, Rabe K M, Adeagbo W A and Acet M 2005 Phys. Rev. B 72 054113
[27] Paul S, Sanyal B and Ghosh S 2015 J. Phys.: Condens. Matter 27 035401
[28] Ivanov O A, Solina I V, Demshira V A and Magat L M 1973 Phys. Met. Metall. 35 92
[29] Fichtner T, Wang C, Levin A, Kreiner G, Mejia C, Fabbrici S, Albertini F and Felser C 2015 Metals 5 484
[30] Gabor M S, Petrisor T, Tsusan C, Hahn M and Petrisor T 2011 Phys. Rev. B 84 134413
[31] Husain S, Akansel S, Kumar A, Svedlindh P and Chaudhary S 2016 Sci. Rep. 432 28692
[32] Zhang M, Brück E, de Boer F R, Li Z and Wu G 2004 J. Phys. D: Appl. Phys. 37 2049
[33] Uvarov N, Kudryavtsev Y, Kravets A, Vovk Y, Borges R, Godinho M and Korenivski V 2012 J. Appl. Phys. 112 063909
[34] Zhang Y J, Wang W H, Zhang H G, Liu E K, Ma R S and Wu G H 2013 Physica B 408 2049
[35] Buschow K, van Engen P and Jongebreur R 1983 J. Magn. Magn. Mater. 38 1
[36] Csand X, Csorgo T and Lorstad B 2004 Nukleonika 49 S49
[37] Ren Z, Li S T and Luo H Z 2010 Physica B 405 2840