Magnetism in tetragonal manganese-rich Heusler compounds

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A comprehensive study of the total energy of manganese-rich Heusler compounds using density functional theory is presented. Starting from a large set of cubic parent systems, the response to tetragonal distortions is studied in detail. We single out the systems that remain cubic from those that most likely become tetragonal. The driving force of the tetragonal distortion and its effect on the magnetic properties, especially where they deviate from the Slater–Pauling rule, as well as the trends in the Curie temperatures, are highlighted. By means of partial densities of states, the electronic structural changes reveal the microscopic origin of the observed trends. We focus our attention on the magnetocrystraline anisotropy and find astonishingly high values for tetragonal Heusler compounds containing heavy transition metals accompanied by low magnetic moments, which indicates that these materials are promising candidates for spin-transfer torque magnetization-switching applications.

I. INTRODUCTION

The spintronics community demands materials with uniaxial anisotropy for spin transfer torque–random access memory (STT-RAM) applications, as well as for fundamental skyrmion-related research or in the field of magnetic shape-memory alloys [1]. Such materials are needed to improve the functionality and applicability of modern devices or device concepts within the scope of mass production or proof of practicality. Addressing this request withing the class of compounds with Heusler and Heusler-like structures, the task is approached by means of relatives of familiar systems [2, 3]. These relatives are the family of Mn2-based Heusler compounds, the famous pioneering material and ancestor of which is Mn3Ga [4, 5]. The uniaxial magnetocrystalline anisotropy of Mn3Ga has been calculated [6] and measured [7] several times on different occasions. It is thought that anisotropic materials such as these could constitute the foundation for magnetic racetrack memory as proposed by Parkin et al. [8]. The indispensable perpendicular magnetic anisotropy (PMA) in (ultra-)thin structures is best controlled by intrinsic properties rather than by shape- or strain-induced anisotropy. As a result, the perpendicular orientation of magnetization is a desired property of the material. Recently, Mn2-based Heusler systems, Mn2YZ, were reconsidered as promising materials. Thus, considerable research has been done on related systems. Mn2NiGa in particular is a well-studied material as it is directly related to Ni2MnGa, which has been the most studied and best understood ferromagnetic shape-memory alloy since its discovery [9, 10]. Mn2NiGa, however, is a ferrimagnetic shape-memory alloy that is theoretically linked to Ni2MnGa through a substitution series, with a transition from ferro- to ferrimagnetic ordering due to the increasing manganese content. In addition to Mn2NiGa, other Mn2-based Heusler alloys have been synthesized and characterized or have been theoretically treated, such as Mn2CoGa [11–15], Mn2FeGa [16], and Mn3Ga [4, 7]. In addition to materials in which Y is an atom from period IV (or the 3d series), equivalent systems with heavier constituents as Y species have been investigated. Among these were Mn2RuGa [17] (which has been found to have more or less random occupation of sites), Mn2RhGa [18] (cubic, disordered), Mn2PtGa [19, 20], and Mn2PdIn [21], in the context of large exchange bias effects. Although a detailed study of a single material is an important task that results in valuable knowledge, the inclusion of cluster knowledge into a general concept creates comprehensive insight. The same intention that guided our previous work [15] motivated us to undertake a similar approach in the current study, i.e., comprehensively studying a selected set of systems. We intend to understand the general trends governing the formation and magnetism of tetragonal materials for the aforementioned applications.

In this paper, we show how the magnetism and the atomic structure change within the Mn2Y(3d)Ga, Mn2Y(4d)Ga, and Mn2Y(5d)Ga series. The trigger quantities causing the tetragonal distortion, as well as the consequences of this distortion, i.e., the magnetocrystalline anisotropy (MCA) [3], will be highlighted and placed into an appropriate context.

II. CRYSTAL STRUCTURE

Heusler alloys are nowadays informally divided into two structure types, the so-called regular and inverse types, referring to the original Heusler compound Cu2MnAl as the reference system [22]. The materials first associated with the name of Fritz Heusler were cubic phases analogous to Cu2MnAl, with the stoichiometry X2YZ. From then on, similar materials were thus labeled “Heusler compound”, extending the original definition of Heusler compounds to the family of Heusler materials that incorporates a variety of similar structures. These structures are derived from the original compound, with occupation of the Wyckoff positions, 8c, 4b, and 4a, in
FIG. 1. (Color online) The conversion from a (a) cubic Heusler structure to a (b) tetragonal derivative phase is displayed in terms of a non-displasive transformation for a system with the general composition of $XX'YZ$ ($X$, $X'$, $Y$ - transition metals and $Z$ - main-group element, marked as red, orange, blue, and green, respectively) within the fcc lattice. (c) Relationship of the lattice parameters as $a_{\text{tet}} = a_{\text{cub}}/\sqrt{2}$.

Heusler materials are generally understood to be intermetallic compounds, distinguishing them from general intermetallics which are forming a broad range of solid solutions, with no preferred but statistical occupation of crystallographic sites. They are also set apart from other ionic or covalent compounds because Heusler systems allow the formation of substitutional series of single sites. However, they maintain the character of an ionic or covalent compound, and thus they are on the borderline between alloys and compounds. Some distinct systems exhibit a tendency to form alloys, nevertheless. The general composition is given by $XX'YZ$, where the classical definition has been widened to incorporate quaternary materials within the family of Heusler compounds. In the representation of SG 216 ($F43m$), the structure contains four highly symmetric Wyckoff positions: $4d$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), $4c$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), $4b$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), and $4a$ ($0, 0, 0$). Depending on the occupation of the crystallographic positions, two ordering possibilities for ternary alloys ($X = X'$) are obtained (Table I). In this study, gallium was chosen as the $Z$ element, whereas one manganese atom, $X$, occupies position $4d$. The second manganese atom, $X'$, and the other transition metal, $Y$, are located at $4c$ or $4b$, respectively, depending on the formation of the regular- or inverse-type Heusler material, as shown in Table I. Other Heusler-related structures [23] are the tetragonal derivatives of the cubic parent phases, which have been widely treated in the context of magnetic shape-memory alloys. The relationship and the unit cell transformation between cubic and tetragonal phases is depicted in Fig. 1.

It is seen that a conventional cubic unit cell can be described in terms of a tetragonal lattice exhibiting a $c/a$ ratio of $\sqrt{2}$. The cell parameters are interrelated according to $c_{\text{tet}} = c_{\text{cub}}$, $a_{\text{tet}} = a_{\text{cub}}/\sqrt{2}$. In this study, a set of Mn$_2$-based materials, including transition metals of periods IV, V, and VI, are considered, namely, Mn$_2$Y$^{(3d)}$Ga, Mn$_2$Y$^{(4d)}$Ga, and Mn$_2$Y$^{(5d)}$Ga.

### III. COMPUTATIONAL DETAILS

The numerical work was done within density functional theory as implemented in the all-electron FP-LAPW code, WIEN2k [24], employing the generalized gradient approximation (GGA) in the parametrization of Perdew, Burke, and Ernzerhof as exchange-correlation functional [25]. The angular momentum truncation was set to $l_{\text{max}} = 9$ and the number of plane-waves determined by $R_{\text{Kmax}} = 9$ to ensure well-converged calculations. The energy convergence criterion for the self-consistent field calculations was set to $10^{-5}$ Ry, whereas the charge convergence was set to $10^{-3}$. All calculations were done on a $20 \times 20 \times 20$ $k$-mesh. For a set of given $c/a$ ratios, the volumes were optimized and fitted to the Birch–Murnaghan equation of state [26, 27]. From these, the optimal ratio and volume were obtained and the lattice parameters evaluated. On the basis of the crystallographic details, complex magnetic properties such as the exchange parameters and the corresponding Curie temperatures ($T_C$) were computed by means of the Korringa–Kohn–Rostoker (KKR) Green’s function method as implemented by the Munich SPR-KKR package [28].

### TABLE I. The structural relationship of the regular and inverse structure types for Mn$_2$YGa is shown, where $X=X'=\text{Mn}$ and $Z=\text{Ga}$, as compared to Fig. 1. Only one possible configuration of a half-Heusler type is listed exemplary.

| Heusler | SG   | 4d   | 4c   | 4b   | 4a   |
|--------|------|------|------|------|------|
| regular | L2$_1$ | 225  | Mn   | Mn   | Y    | Ga   |
| inverse | X$_a$ | 216  | Mn   | Y    | Mn   | Ga   |
| half   | Cl$_b$ | 216  | Mn   | Mn   |      | Ga   |

The spacegroup (SG) 225 through the introduction of vacancies or slight structural changes. These modifications alter the structure by breaking the inversion symmetry when going from a regular Heusler phase to an inverse or half-Heusler structure.
angular momentum expansion was truncated for $l_{\text{max}} = 3$ which corresponds to the $f$-wave symmetry. The energy integration was done on a complex energy mesh with 48 points along the integration path, using the Lloyd’s formula [29] for an improved estimate of the Fermi energy. The computation of the exchange parameters is based on the classical Heisenberg model, which was evaluated by means of the real-space approach [30]. This provides site- and distance-dependent exchange between sites via infinitesimal rotation of the magnetic moments at a particular site in real space. To account for distance dependence, an appropriate truncation of the cluster radius, $r$, around each atomic site had been chosen. This radius was set to $3.5 \, a$ lattice spacings to capture even small interactions, as the largest contributions to the effective exchange constants are found for radii smaller than $1.5 \, a$ lattice spacings [15, 31].

IV. RESULTS

A. Lattice Relaxation

The total energy $E(c/a)$ as a function of the $c/a$ ratio was calculated and the results are shown in Figs. 2–5. The energy zero are defined with respect to the cubic parent compound, and consequently the energy difference for all phases can be compared easily. The case of $\text{Mn}_2\text{Ga}$ is used as a benchmark and is repeatedly plotted in Figs. 2 and 3. Table III contains the numerically optimized lattice parameters. The study reveals that a large number of the herein-treated materials are most stable in their respective tetragonal structures, with $c/a > \sqrt{2}$. Tetragonally compressed structures are described by $c/a < \sqrt{2}$, whereas tetragonally elongated lattices are characterized by $c/a > \sqrt{2}$, as compared to the cubic parent or austenite phase. Elongation occurs with an increase in the length of the $c$-axis, whereas the $ab$-plane is compressed, leaving the volume approximately unchanged. In this study, the volume of the unit cell, $V_{\text{cell}}$, was optimized in addition to the $c/a$-ratio, and it was found that no significant change occurred for most cases (Table II).

Figs. 2a and 2b show the $E(c/a)$ curves of the

![Graph showing the energetic response to volume-conserving elongations and compressions of the crystal structure along the $c$-axis for the Mn$_2$Y(3$d$)Ga-series. Panel (a) includes systems with a valence electron count $N_v(Y) \leq 7$ (early transition metals, ETM) and panel (b) shows the remaining combinations of Mn$_2$Y(3$d$)Ga with $N_v(Y) \geq 7$, with so-called late transition metals (LTM).](image-url)
Y = Mn, Fe, Co, Ni, Cu), respectively. A preference for tetragonal structures is seen for materials including LTM for Mn$_2$Y$^{(4d)}$Ga, with Y being Mn, Fe, or Ni. In the group of ETM systems, Mn$_2$SeGa was found to be tetragonal, which is an exception. The situation for Mn$_2$Y$^2$Ga and Mn$_2$Y$^{(5d)}$Ga is seen to be similar.

In contrast to Mn$_2$CoGa, for which a cubic structure ($c/a = \sqrt{2}$) is preferred, the systems with the same valence electron count ($N_v = 26$) involving heavier species (ruthenium and osmium) exhibit a global energy minimum for the tetragonal structure.

Discontinuities in the $E(c/a)$ curves are observed for the cases of Mn$_2$Ga and Mn$_2$FeGa, resembling a first-order transition, whereas $E(c/a)$ for Mn$_2$NiGa is continuous (Fig. 2b). Strongly composition-dependent modulated martensitic phases [32, 33] and premartensitic phases [34, 35] have been experimentally produced; in combination with first-principles calculations [36], the onset of the martensitic transition has been thought to be initiated by a displacement of atomic planes orthogonal to the crystallographic $c$-axis of the tetragonal cell. Experimentally [35] and theoretically [36], it has been shown that phonon softening along $[\zeta, \zeta, 0]$ exists in shape-memory materials, and thus the transition has been related to the occurrence of the tetragonal distortion.

The approach undertaken in the current study resulted in elongated structures in those cases, which were unstable towards a tetragonal distortion. Additionally, global energy minima for distorted phases were found mostly for the inverse structures, as depicted in Fig. 4. In contrast, compressed variants possessing a global energy minimum were not observed in the Mn–Ga Heusler family. The calculated lattice data and the figures shown (Figs. 2–3) lead to the conclusion that stable tetragonal structures may only be formed in the series of Mn$_2$YGa that includes LTMs, making them derivatives of inverse Heusler systems. The information obtained from the lattice optimization in terms of the relative positions of the energy minima is condensed in Fig. 4, which gives the preferred crystal structure visualized in the manner of the periodic table.

Each compound in the family of Mn$_2$YGa materials shown in this figure is depicted by one cell that symbolizes a transition metal $Y$ of the 3$d$, 4$d$, or 5$d$ series. The corresponding cell is built up by three subcells, which represent the two variants of chemical coordination (the first or second subcell) and the existence of a global energy minimum for $c/a \neq \sqrt{2}$ (third subcell). The color code symbolizes the energy level of a configuration on the energy landscape relative to one another: dark green - global minimum, light green - local minimum, red - no minimum. In cases in which the investigated materials did not exhibit a cubic minimum, the first two subcells are understood to be the type of coordination around the 4$d$ crystallographic site: the symmetry of the coordinating shell is either centrosymmetric (in relation to SG 225) or non-centrosymmetric (in relation to SG 216). As shown in a preceding publication on the cubic variants [15], systems involving ETMs adopt the L2$_1$-type structure, whereas compounds containing LTMs are found to have the inverse Heusler structure (X$_{\sigma}$-type).

Inspection of Fig. 4 in combination with Figs. 2 and 3 reveals interesting details, such as the fact that tetragonal derivative phases of cubic Heusler alloys, implying that a global energy minimum is present, are observed only for a valence electron count of $N_v \geq 24$. It is also clearly seen that the onset of the formation of tetragonally elongated structures evolves over the periods from
left to right and from lower to higher $N_V$.

This leads to the question of the mechanism behind this distortion, which we are going to approach in Sec. IV A 1. The lattice parameters for all cubic compounds are found within a range of $\Delta a/\sqrt{a} < 0.35$ Å for the Ga series. The values increase from the borders of the series towards the middle of the range. The same behavior is found for tetragonal compounds, where the range spans from $a_{tet} = 3.68$ to 4.11 ($\Delta a_{tet} = 0.43$ Å) and $c_{tet} = 6.91$ to 7.48 ($\Delta c_{tet} = 0.54$ Å), whereas Mn$_2$ScGa is an exception. The $c/a$ coordinate exhibits inverted behavior, decreasing from the middle to the left and right borders of the series. The overall similarity of the lattice data opens the possibility of intermixability with each other and thus tunability of the whole class of materials. Therefore, the magnetization may be adjusted over a large range, allowing for the formation of tetragonal compensated ferrimagnets via adequate substitution.

Having discussed the structural trends as a function of the valence electron change in the $d$-electron system, the effects of the variation of the main group element, $Z$, from Ga to Ge, In, and Sn in a small sample of compounds [Mn$_2$(Mn,Fe)Ge, Mn$_2$(Os,Ir,Pt)In, and Mn$_2$(Os,Ir,Pt)Sn] are briefly discussed. The corresponding data, including those for Mn$_2$Ga, are graphed in Fig. 5.

Fig. 5 reveals that the emergence of a deep energy minimum for Mn$_2$IrSn with $c/a < \sqrt{2}$ and even deeper minima for elongated phases with large $c/a$-ratios of Mn$_2$OsIn, Mn$_2$IrIn and Mn$_2$OsSn whose lattice parameters resemble those of layered structures. Heusler alloys are often interpreted in terms of a rigid, band model-like approach, and an electron-filling scheme is employed for the prediction of magnetic moments in Co$_2$-based alloys. Interpretation of the tetragonal instabilities using such an approach leads to the assumption of Mn$_2$Ge ($N_V = 25$) behaving analogously to Mn$_2$FeGa ($N_V = 25$) and of Mn$_2$FeGe ($N_V = 26$) being similar to Mn$_2$CoGa ($N_V = 26$). A comparison of the corresponding $c/a$ curves demonstrates that this is approximately true and thus that isoelectronicity is an appropriate concept in the chemistry and physics of Heusler materials.

Although our calculations agree well with those of previous works [37], comparison with the experimental data of Mn–Ni–Ga systems exhibits an interesting discrepancy. The deviation between experiment and theory was traced back to the deviating structural model in terms of the occupation of the involved sites. Neutron diffraction studies on Mn$_2$NiGa highlighted the fact that the order is different from the expected $X_a$-type in the austenitic phase. Thus, the chemical formula reads as (Mn,Ni)$_2$MnGa and is called L$_{21}$-type because the point symmetry includes inversion symmetry through random occupation of $4c$ sites with Ni and Mn [38]. Similarly in Mn$_2$FeGa, a deviation from theory was found in an experimental study because the site occupation was expected to differ from the perfect MnFeMnGa ordering [16]. Similar issues are present for the Mn$_2$Y(4d)Ga series. From available data, including neutron diffraction studies, the site occupancies have been clarified. Several authors found that members of the Mn$_2$RuZ series ($Z = \text{Ga}$, Ge, Si, Sn) and Mn$_2$RhZ series ($Z = \text{Ga}$) [17, 18, 39] not to be tetragonal under the respective reaction conditions. In contrast, they have been realized as cubic Heusler alloys exhibiting a strong degree of anti-site disorder, which has been characterized as an alloying tendency [18].

Orthorhombic deformations of the unit cell have been observed in some systems such as Mn$_2$NiGa [37]. Thus, the restriction to tetragonal distortions and ordered compounds in conducted studies leads to a simplified description of these materials. Nevertheless, a general understanding can be obtained in approaching the Mn$_2$-based Heusler systems through this ansatz. In future studies...

![Diagram](image-url)
that aim to predict ground-state structures and magnetic configurations, the parameter space for the atomic sites and relaxations paths for the electronic and spin degrees of freedom has to be enlarged and restrictions that are widely used have to be dropped. As a consequence of the applied restrictions, disorder effects were not incorporated into this study, thus leaving open any explanations of the deviations from experimental results.

1. Analysis of the Densities of States

Various attempts to explain the instability of the cubic phase have been given in the literature using models such as the band Jahn–Teller effect [5, 16], anomalous phonon vibrations [49, 50], and Fermi-surface nesting [51]. These different approaches describe the same behavior, i.e., the instability of the cubic phase, from different perspectives and extracting different types of information. Commonly, the densities of states (DOSs) of related austenite and martensite are compared and contrasted marking the starting and the endpoint of the transition. As example for the Mn$_2$Y$^{(3d)}$Z series, the DOSs of Mn$_3$Ga, Mn$_2$FeGe, and Mn$_2$NiGa are shown in Figs. 6–8. For the cubic variants, the partial DOSs (PDOSs) are shown in their corresponding projections on the sites and in terms of projections on the irreducible representations. The peaks in the PDOS of Mn(4b) are well separated on the energy scale. On the one hand, this separation is due to the strong crystal field splitting of the Mn(4b) $d$-states, where the occupied $e_g$ states are located in a range between $-4$ and $-3$ eV, whereas the $t_{2g}$ PDOS is found between $-1$ eV and the Fermi edge, $\varepsilon_F$. On the other hand, the separation of occupied and empty states follows from the strong exchange split of the Mn(4b) $d$-states, in contrast to the $d$-states of Y(4c) and Mn(4d), which are found to be more widely dispersed even though the majority and minority states are separated owing to exchange splitting. The PDOSs of Mn(4d) and Y(4c) are strongly dispersed, with considerable overlap of the spectral weight between the $t_{2g}$ and $e_g$ states in the majority channel, whereas the minority channel is gapped, with $t_{2g}$ characterizing the lower boundary and $e_g$ comprising the upper boundary of the gap. As the DOS is gapped in the minority spin channel the study of the tetragonal system is strongly facilitated as the states at the Fermi edge in the majority channel mostly constitute the origin of the tetragonal distortion. The majority PDOSs in the range of $-5$ eV up to $\varepsilon_F$ exhibit a characteristically shaped peak structure. From Mn$_3$Ga to Mn$_2$CoGa, the majority spin channel (lower panels of Figs. 6a–8c) is continuously filled. The Fermi energy is consequently shifted to higher band energies and thus $\varepsilon_F$ sweeps over a range of the majority DOSs, whereas the minority spin channel remains unchanged. It is clearly seen from Figs. 6 and 7 that the tetragonal transition correlates with the peak structure of the majority DOSs. For $\varepsilon_F$ being centered on a peak of the majority DOS, the tetragonal distortion can be triggered. These local maxima are mainly composed of states of the $Y(4c)$ (Mn, Fe, Co, Ni) and Mn (4d) atoms. These energy levels are of $t_{2g}$ symmetry mainly. In simple interpretation, the DOS can be understood in a rigid-band-like fashion. The limit of this interpretation is reached with Mn$_2$NiGa, where the $d$-PDOS is rearranged and the Slater–Pauling rule is no longer valid for the cubic phase [15]. Comparing this to the PDOSs of the tetragonally distorted systems, it is observed that the resulting PDOSs are widely dispersed and significantly less structured. Mn$_2$NiGa, however, behaves differently. Further filling of the majority states, as intuitively expected, does not occur. In contrast, the gap in the minority channel closes as the states of $e_g$ symmetry are pulled towards $\varepsilon_F$. Thus, the tetragonal distortion in Mn$_2$NiGa is formed by another mechanism, which may explain why Mn$_2$NiGa is found to be a magnetic shape memory alloy, whereas Mn$_3$Ga and Mn$_2$FeGa are found in their respective tetragonal crystal structures, although the total energy differences are comparable to that of Mn$_2$NiGa.

We emphasize that these findings differ from other models in which the instability is thought to depend solely on states of Mn(4b) that is found in a tetrahedral environment. The DOS at $\varepsilon_F$ in mainly composed of states of the 4c and 4d positions with minor contributions from Mn(4b). Here the instability removes the strong peaks of Mn, Fe, and Co at the 4c position, whereas the states of Mn(4b) are not rearranged.

2. Spin-Polarization

Half-metallicity [52, 53] (complete or nearly complete spin-polarization $F(\varepsilon_F) \approx 100\%$) is generally observed in cubic Co$_2$- and Mn$_2$-based Heusler compounds. The
TABLE III. Calculated lattice parameters of the cubic parent phases and corresponding tetragonal structures, in comparison with existing literature data. The lattice parameters are given in Angstroms. The saturation magnetization data, $M_S$, are given in $\mu_B$ / f.u. The listed literature data refer to theoretical (x) or experimental (xo) investigation of the mentioned cubic (c) or tetragonal (t) phases, respectively.

| $N_y$ | SG | $c/a$ | $a_x$ | $a_t$ | $M_S$ | SG | $c/a$ | $a_t$ | $c_t$ | $M_S$ | ordering | Lit. |
|-------|----|-------|-------|-------|-------|----|-------|-------|-------|-------|---------|-----|
| Mn$_2$ScGa 20 | 225 | $\sqrt[7]{2}$ | 6.15 | 4.35 | $-4.00$ | 139 | 1.94 | 3.98 | 7.70 | $-5.36$ |
| Mn$_2$TiGa 21 | 225 | $\sqrt[7]{2}$ | 5.95 | 4.21 | $-2.97$ | 139 | 225 | $\sqrt[7]{2}$ | 5.95 | ct MnMnTiGa | [40] |
| Mn$_2$VGa 22 | 225 | $\sqrt[7]{2}$ | 5.82 | 4.12 | $-1.98$ | 139 | 225 | $\sqrt[7]{2}$ | 5.91 | ce MnMnVGa | [41],[42] |
| Mn$_2$CrGa 23 | 225 | $\sqrt[7]{2}$ | 5.76 | 4.07 | $-1.00$ | 139 | 1.82 | 3.82 | 6.95 | $-2.75$ | 225 | $\sqrt[7]{2}$ | 5.77 | ct MnMnCrGa | [43] |
| Mn$_2$Ga 24 | 225 | $\sqrt[7]{2}$ | 5.82 | 4.12 | 0.01 | 139 | 1.82 | 3.90 | 7.08 | $-1.89$ | 139 | 1.77 | 3.77 | 7.16 | ct MnMnMnGa | [4] |
| Mn$_2$FeGa 25 | 216 | $\sqrt[7]{2}$ | 5.79 | 4.09 | 1.03 | 119 | 1.98 | 3.68 | 7.29 | $-0.78$ | 119 | 1.90 | 3.79 | 7.19 | te Mn(Fe,Mn)$_2$Ga | [16] |
| Mn$_2$CoGa 26 | 216 | $\sqrt[7]{2}$ | 5.78 | 4.09 | 2.00 | 119 | 1.93 | 3.71 | 7.14 | 0.17 | 216 | $\sqrt[7]{2}$ | 5.86 | ce MnCoMnGa | [44] |
| Mn$_2$NiGa 27 | 216 | $\sqrt[7]{2}$ | 5.85 | 4.14 | 1.18 | 119 | 1.82 | 3.79 | 6.91 | 1.00 | 216 | $\sqrt[7]{2}$ | 5.91 | ce | [45] |
| Mn$_2$CuGa 28 | 216 | $\sqrt[7]{2}$ | 5.94 | 4.20 | 0.33 |
| Mn$_2$ZrGa 21 | 225 | $\sqrt[7]{2}$ | 6.14 | 4.34 | $-3.00$ |
| Mn$_2$NbGa 22 | 225 | $\sqrt[7]{2}$ | 6.00 | 4.24 | $-2.00$ |
| Mn$_2$MoGa 23 | 225 | $\sqrt[7]{2}$ | 5.91 | 4.18 | $-1.01$ | 119 | 1.81 | 3.89 | 7.04 | $-2.99$ |
| Mn$_2$RuGa 25 | 216 | $\sqrt[7]{2}$ | 5.96 | 4.22 | 1.03 | 119 | 1.96 | 3.80 | 7.45 | $-0.24$ | 216 | $\sqrt[7]{2}$ | 6.00 | ce (Mn$_2$,Ru$_2$)$_3$Ga | [17] |
| Mn$_2$RhGa 26 | 216 | $\sqrt[7]{2}$ | 5.98 | 4.23 | 1.64 | 119 | 1.94 | 3.82 | 7.43 | 0.10 | 225 | $\sqrt[7]{2}$ | 6.03 | ce (Mn,Rh)$_2$MnGa | [18] |
| Mn$_2$PdGa 27 | 216 | $\sqrt[7]{2}$ | 6.12 | 4.33 | 0.55 | 119 | 1.84 | 3.93 | 7.23 | 0.93 |
| Mn$_2$AgGa 28 | 216 | $\sqrt[7]{2}$ | 6.22 | 4.40 | 0.34 |
| Mn$_2$HfGa 21 | 225 | $\sqrt[7]{2}$ | 6.12 | 4.33 | $-2.99$ |
| Mn$_2$TaGa 22 | 225 | $\sqrt[7]{2}$ | 6.00 | 4.24 | $-1.99$ |
| Mn$_2$WGa 23 | 225 | $\sqrt[7]{2}$ | 5.92 | 4.19 | $-0.94$ |
| Mn$_2$OsGa 25 | 216 | $\sqrt[7]{2}$ | 5.95 | 4.21 | 1.02 | 119 | 1.97 | 3.80 | 7.48 | $-0.28$ |
| Mn$_2$IrGa 26 | 216 | $\sqrt[7]{2}$ | 5.97 | 4.22 | 2.00 | 119 | 1.95 | 3.83 | 7.44 | 0.11 |
| Mn$_2$PtGa 27 | 216 | $\sqrt[7]{2}$ | 6.13 | 4.33 | 0.44 | 119 | 1.87 | 3.91 | 7.31 | 0.75 | 119 | 1.38 | 4.37 | 6.05 | te MnPtMnGa | [19] |
| Mn$_2$AuGa 28 | 216 | $\sqrt[7]{2}$ | 6.26 | 4.42 | 0.19 | 119 | 1.73 | 4.11 | 7.13 | 0.14 |
| Mn$_2$OsSn 25 | 216 | $\sqrt[7]{2}$ | 6.21 | 4.39 | 1.50 | 119 | 1.95 | 3.97 | 7.75 | $-0.02$ |
| Mn$_2$IrSn 26 | 216 | $\sqrt[7]{2}$ | 6.31 | 4.46 | 0.41 | 119 | 1.91 | 4.01 | 7.67 | 0.45 | 119 | 1.54 | 4.29 | 6.59 | te MnIrMnSn | [46] |
| Mn$_2$PtSn 27 | 216 | $\sqrt[7]{2}$ | 6.39 | 4.52 | 0.19 | 119 | 1.81 | 4.15 | 7.52 | $-0.02$ | 119 | 1.35 | 4.51 | 6.08 | te MnPtMnSn | [1] |
| Mn$_2$OsIn 25 | 216 | $\sqrt[7]{2}$ | 6.26 | 4.43 | 0.62 | 119 | 2.02 | 3.93 | 7.93 | $-0.27$ |
| Mn$_2$IrIn 26 | 216 | $\sqrt[7]{2}$ | 6.30 | 4.45 | 0.68 | 119 | 1.98 | 3.97 | 7.85 | 0.07 |
| Mn$_2$PtIn 27 | 216 | $\sqrt[7]{2}$ | 6.37 | 4.51 | 0.31 | 119 | 1.84 | 4.12 | 7.57 | 0.38 | 119 | 1.57 | 4.32 | 6.77 | te MnPtMnIn | [21] |
| Mn$_3$Ge 25 | 216 | $\sqrt[7]{2}$ | 5.76 | 4.07 | 1.01 | 119 | 1.90 | 3.74 | 7.10 | $-0.98$ | 225 | 1.91 | 3.81 | 7.26 | te MnMnMnGe | [47] |
| Mn$_2$FeGe 26 | 216 | $\sqrt[7]{2}$ | 5.73 | 4.05 | 2.01 | 119 | 2.05 | 3.63 | 7.42 | $-0.06$ | 216 | $\sqrt[7]{2}$ | 5.80 | ct MnFeMnFe | [48] |

The highly symmetric structure and the peculiar electronic properties due to covalent bonding lead to the appearance of a gap in the minority density of states (DOS). The emergence of the tetragonal distortion reduces the spin-polarization of the half-metallic cubic parent phases. The degeneracy of the $t_{2g}$ and $e_g$ states is lifted due to the change in local coordination caused by the distortion, which is seen in Figs. 6–8 and Fig. 16, and the emergence of a pseudo-gap in one spin-channel is observed instead.
FIG. 6. (Color online) DOS of cubic (SG 225) and tetragonal (SG 139) Mn$_3$Ga.

B. Magnetic Ground State

1. The Slater–Pauling Rule

Referring to a previous publication [15] on the cubic parent compounds of the investigated materials, the results are presented by means of the Slater–Pauling curves. As can be seen in Fig. 10, the Slater–Pauling rule experiences strong changes, so that calling it the Slater–Pauling rule is done for reasons of convenience. Fig. 10 visualizes the fact that the magnetization of all tetragonal alloys of the Mn$_2$Y$^{(d)}$Ga family experiences a shift to smaller values. In the case of the Mn$_2$Y$^{(3d)}$Ga group, this shift is found to be constant throughout the set of compounds, which results in a linear dependence of the net moment on the valence electron count, thus giving rise to pseudo-Slater–Pauling behavior, even though half-metallicity and thus integer net moments are not observed (Fig. 9). A decrease of the net moment is also found for the Mn$_2$Y$^{(4d)}$Ga and Mn$_2$Y$^{(5d)}$Ga compounds. Unlike the lighter compounds, the changes are not constant over the series and therefore result in nearly vanishing net moments for Mn$_2$RuGa, Mn$_2$RhGa, Mn$_2$PdGa, Mn$_2$OsGa, Mn$_2$IrGa, Mn$_2$PtGa, and Mn$_2$AuGa, as is seen in Fig. 10. Nevertheless, compensation of spin moments may be achieved for an electron count close to $N_V = 25.7$, which can be realized by intermixtures of stoichiometric phases of Mn$_2$YGa, such as $m_{Mn_2Ga} = -1.89 \mu_B$ and a corresponding proportion of Mn$_2$NiGa with $m_{Mn_2NiGa} = 1.00 \mu_B$ or Mn$_2$CoGa.

FIG. 7. (Color online) DOS of cubic (SG 216) and tetragonal (SG 119) Mn$_2$FeGa.
Thus, fractions of 0.435 \( m_{\text{Mn}_2\text{NiGa}} \) and 0.565 \( m_{\text{Mn}_2\text{FeGa}} \) could ideally lead to complete compensation of the magnetization. A similar approach was undertaken by Nayak et al. that obtained a compensated ferrimagnet by varying the Mn/Pt-ratio in \( \text{Mn}_3-x\text{Pt}_x\text{Ga} \) leading to complete compensation of magnetization for \( x \approx 0.59 \) theoretically [54]. In \( \text{Mn}_2\text{Ru}_x\text{Ga} \) thin films the compensation of the spin-moment has been achieved through variation of the ruthenium concentration [54].
The change of the total magnetic moment is to be understood in terms of the site moments. Inspection of Fig. 11 clearly reveals the dependencies. The change in the local moments indicates the specific impact of the distortion on the single sites. The local moments responding strongest to elongation/compression of the crystal axes are members of the magnetic sublattices formed by the Mn(8c), Mn(4d), and Y(4c) sites (the former so-called tetrahedral sites as compared to SG 225). Depending on the characters of the local moments, which are either itinerant or localized in nature [12, 52], we find major differences in the influence of the tetragonal distortion on these sites. In Fig. 11, the localized moment of Mn(4b) is found in the upper part of the plot for a positive value of the magnetic moment of approximately 3 $\mu_B$. The effect of elongation along the $c$-axis and compression of the $ab$-plane has a stronger influence on moments of itinerant character found in the lower part of the plot, referring to the $4d$ and $4c$ sites. These are located in the same lattice plane (compare the atoms depicted as red and blue spheres in Fig. 1). Manganese on site 4b [Mn(4b)] exhibits a large localized moment of 3 $\mu_B$, is thus generally less affected. Apart from the magnitude of the local moments, Fe(4c) in Mn$_2$FeGa exhibits a spin-flip from parallel to anti-parallel alignment of the Mn(4b)-Fe(4c) interaction upon the tetragonal distortion. Apart from the changes in magnitude of the local atomic moments, the effective anti-parallel coupling of the nearest neighbor manganese atoms does not suffer from the structural transformation, as will be quantified in terms of the exchange interaction constants in Sec. IV C. Since the volume change $C_{t/c}$ is in the order of 1-2% for the most systems, the nearest-neighbor distance basically does not change, whereas the direction of the nearest-neighbor interaction does (Fig. 16). In the case of Mn$_3$Ga, $C_{t/c}$ is approximately 9%, and thus may suppress the shape memory effect in this material.

4. Magnetocrystalline Anisotropy

Inherent in noncubic crystals is a directional preference of magnetization that is absent in cubic materials, which is related to the tetragonal modification of the crystal axes. The magnetocrystalline anisotropy (MCA) energy is here defined as the energy difference between states with magnetization pointing along the $z$-axis and the $x$- or $y$-axis, that is, $E_{MCA} = E_{(100)} - E_{(001)}$, whereas other crystallographic directions are not considered. The anisotropy energy is phenomenologically thought to depend on the value of the $c/a$ ratio, which is more or less equal for most of the compounds investigated in the present study. Therefore, the underlying mechanism is understood as a band-filling effect, which affects the spin orbit coupling (SOC) symmetry. This interpretation can be directly taken from Figs. 12 and 13. Increasing the SOC strength by varying the $Y$ element through the 3d, 4d, and 5d series increases the MCA energy by a factor of approximately 3 for $Y = Fe, Ru, Os$. The effect of band filling is deciphered by sweeping the $Y$ elements along a series. Going from left to right in any set of compounds Mn$_2$Y$(\text{3d})$Ga, the MCA is altered from preferred out-of-plane to in-plane orientation. The same situation holds for Mn$_2$Y$(\text{5d})Z$ compounds, whose preferred orientation is graphed in Fig. 13. Two compounds in this figure deserve special attention, which are Mn$_2$PtIn and Mn$_2$IrSn.
Previously they were predicted to possess a non-collinear magnetic order just as $\text{Mn}_2\text{RhSn}$, which was described in great detail in Ref. [46]. Although we did not consider non-collinear order in the present case, it might be worth while to point out that it is the Mn-atom on site 4$d$ that reacts by canting to the incipient spin-reorientation that is seen clearly in Figs. 12. Similar physics is observed in the famous Rare-Earth magnets $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Er}_2\text{Fe}_{14}\text{B}$. Manganese thus shares properties with Rare Earths [55–57].

C. Exchange Coupling and Curie Temperatures

The details of the calculations pertaining to Curie temperatures ($T_C$) have been described by us previously [15]. Even though the in-plane next-nearest-neighbor distance decreases due to the tetragonal distortion, the next-nearest neighbor Mn(8$c$)-Mn(8$c$) coupling is still positive for the $L_2_1$-derived tetragonal phases; thus, the overall magnetic order does not change. A decrease or change of sign of the coupling constant $J_{\text{Mn}(4d)\text{–Mn}(4d)}$ is typical owing to preferential anti-parallel coupling as caused for short Mn–Mn distances. Instead, the cubic to tetragonal transition even results in increased values, thus leading to an increase of $T_C$. Prima facie, the overall trend of increased $T_C$s cannot be traced back to a common mechanism. In contrast, there is no exchange interaction that exhibits a similar behavior over the series. For instance, the findings in the case of $\text{Mn}_2\text{FeGa}$ are related to the reduction of magnetic frustration, which is due to the competing anti-parallel interaction Mn(4$b$)–Mn(4$d$), and parallel interactions of Fe(4$c$) with both Mn(4$d$) and Mn(4$b$) neighbors. Upon the tetragonal distortion a spin-flip of the Fe(4$c$) local moment is observed, due to the change of the sign of Mn(4$b$)–Fe(4$c$) interaction. Upon the distortion, the strength of Mn(4$b$)–Mn(4$d$) interaction is altered by approximately $\Delta J_{\text{Mn}(4b)\text{–Mn}(4d)} = 56$ meV in $\text{Mn}_2\text{FeGa}$.

A similar, but smaller effect is found in $\text{Mn}_2\text{CoGa}$, indicating the magnetic frustration that had been present in the cubic phase and the weakening of the exchange interaction $Y(4c)$–Mn(4$b$) ($Y=\text{Fe}, \text{Co}$) due to the tetragonal distortion. This might be one of the contributions prohibiting the shape memory effect in $\text{Mn}_2\text{FeGa}$. The main contribution to $T_C$, the Mn(4$d$)–Mn(4$b$) exchange, does not suffer from the structural transition. Similarly, the influence of the distortion on the exchange causes the smaller contributions to be altered and some frustration to be diminished. For example, the Mn(4$d$)–Mn(4$d$) interaction vanishes, with preferred anti-parallel alignment in the cubic case, whereas the major Mn(4$d$)–Mn(4$b$) interaction remains unchanged.

Exceptions to the general observation of increased $T_C$ in tetragonally distorted phases are $\text{Mn}_2\text{NiGa}$, $\text{Mn}_2\text{PdGa}$, and $\text{Mn}_2\text{PtGa}$ systems, in which the $T_C$s are reduced upon the tetragonal distortion. The significant reduction (Fig. 14) is caused by a weakened Mn(4$d$)–Mn(4$b$) interaction (Fig. 15) that may indicate an unstable magnetic groundstate. A relation to the Heusler compound $\text{Mn}_2\text{RhSn}$ [46] can theoretically be established as these materials possess the same number of valence electrons, $N_V$. $\text{Mn}_2\text{RhSn}$ has been shown to exhibit a non-collinear magnetic groundstate due to canting of the different manganese moments [46]. Non-collinear spin configurations have not been considered in this work, so that canting of the spins or spin spiral groundstates in these materials may be present.

V. SUMMARY

Using total energy calculations within density functional theory, we investigated in detail the response to tetragonal distortions for a large set of cubic Heusler compounds, $\text{Mn}_2Y^{(3d,4d,5d)}\text{Ga}$, and some other chosen materials. We were able to single out the systems that remain cubic from those that favor a tetragonal structure. The

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FIG. 12. (Color online) Calculated MCA energy of $\text{Mn}_2\text{YGa}$.

FIG. 13. (Color online) Calculated MCA energy of some chosen $\text{Mn}_2YZ$ alloys: $\text{Mn}_2\text{Ge}$, $\text{Mn}_2\text{IrIn}$, $\text{Mn}_2\text{IrSn}$, $\text{Mn}_2\text{PtIn}$, and $\text{Mn}_2\text{PtSn}$. 

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TABLE IV. The calculated Curie temperatures in Kelvin of tetragonal $T_{C,t}$ and cubic $T_{C,c}$ parent compounds (taken from Ref. 15). The changes due to the tetragonal transformation are listed as $\Delta T_{C,t,c}$. $E_{\text{MCA}}$ represents the magnetocrystalline anisotropy energies in meV per formula unit, whereas the anisotropy constant, $K_u$, is given in $\text{meV}$. 

| Compound | $P_e$ | $P_i$ | $T_{C,c}$ | $T_{C,t}$ | $\Delta T_{C,t,c}$ | $E_{\text{MCA}}$ | $K_u$ |
|----------|-------|-------|-----------|-----------|-------------------|----------------|-------|
| Mn$_2$ScGa | 87 | 35 | 464 | 0.616 | 1.62 |
| Mn$_2$TiGa | 83 | 557 | | | |
| Mn$_2$VGa | 94 | 587 | | | |
| Mn$_2$CrGa | 97 | 50 | 578 | 970 | 392 | 0.779 | 2.46 |
| Mn$_2$Ga | 96 | 56 | 221 | 610 | 389 | 0.906 | 2.7 |
| Mn$_2$FeGa | 95 | 56 | 601 | 848 | 247 | 0.359 | 1.16 |
| Mn$_2$CoGa | 93 | 60 | 928 | 1124 | 196 | 0.236 | 0.77 |
| Mn$_2$NiGa | 35 | 42 | 1005 | 750 | $-255$ | 0.193 | 0.62 |
| Mn$_2$CuGa | 53 | 1491 | | | |
| Mn$_2$ZrGa | 82 | 207 | | | |
| Mn$_2$NbGa | 98 | 289 | | | |
| Mn$_2$MoGa | 85 | 65 | 140 | 335 | 196 | 0.636 | 1.91 |
| Mn$_2$RuGa | 95 | 1 | 619 | 1315 | 696 | 0.564 | 1.68 |
| Mn$_2$RhGa | 15 | 59 | 576 | 1351 | 776 | 0.322 | 0.95 |
| Mn$_2$PdGa | 7 | 46 | 809 | 335 | $-473$ | 0.040 | 0.11 |
| Mn$_2$AgGa | 24 | 1240 | | | |
| Mn$_2$HfGa | 89 | | | | |
| Mn$_2$TaGa | 96 | | | | |
| Mn$_2$WGa | 83 | | | | |
| Mn$_2$OsGa | 96 | 273 | 1075 | 802 | 3.270 | 9.72 |
| Mn$_2$IrGa | 74 | 5 | 411 | 1122 | 711 | 2.388 | 7.02 |
| Mn$_2$PtGa | 23 | 51 | 799 | 326 | $-472$ | $-0.293$ | $-0.84$ |
| Mn$_2$AuGa | 8 | 26 | 1027 | 897 | $-130$ | $-0.731$ | $-1.94$ |

FIG. 14. (Color online) The calculated Curie temperatures of the Heusler compounds containing Ga. The results shown here are obtained in the Mean-Field Approximation (MFA) and highlight the consequence of the structural relaxation. Squares correspond to cubic compounds and rectangles to tetragonal compounds.

FIG. 15. (Color online) The evaluated effective exchange interaction parameters are shown and compared for all cubic and tetragonal cases. Thus, the underlying mechanism of the increase of $T_C$ due to the distortion is visualized. Circles correspond to cubic compounds and rectangles to tetragonal compounds.

FIG. 16. (Color online) A two-dimensional projection of the nearest-neighbor coordination of Mn(4b) is shown. The symmetry of the coordination changes while undergoing the martensitic transition, whereas the nearest-neighbor distance remains unchanged as the volume change is on the order of only 1–9%.

details of the total energy as a function of the distortion were found to be similar for materials exhibiting the same number of valence electrons. The magnetizations of the tetragonal alloys were found to be shifted to smaller values, which we could attribute to changes of the itinerant local moments. This led to characteristic modifications of the Slater–Pauling curve. By means of partial densities of states, the changes to the electronic structures revealed the microscopic origin of the observed trends. As compared to the cubic parent phases, a strengthening of the exchange interaction between neighboring sites was observed, which resulted in an increase of the Curie temperature. Focusing our attention on the magnetocrystalline anisotropy we observed an interesting trend that describes a spin reorientation over our series of com-
pounds, furthermore very large anisotropies are found for tetragonal Heusler compounds containing heavy transition metals accompanied by low magnetic moments, which indicates that these materials may be promising candidates for spin-transfer torque applications.

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