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Heusler compounds with perpendicular magnetic anisotropy and large tunneling magnetoresistance

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In present work we suggest a receipt for finding tetragonal Heusler compounds with perpendicular magnetic anisotropy (PMA) that also exhibit large tunneling magnetoresistance (TMR) when used as electrodes in magnetic tunnel junction (MTJ) devices with suitable tunneling barrier materials. We performed the density-functional theory calculations for 286 Heusler compounds and identified 116 stable tetragonal compounds. Ten of these compounds are predicted to have strong PMA and, simultaneously, exponentially increasing TMR with increasing tunneling barrier thickness due to the so-called Brillouin zone spin filtering effect. Experimental measurements performed for 25 Heusler compounds theoretically identified as tetragonal show that 10 of these compounds indeed have tetragonal structure with PMA. Eight of these compounds are reported for the first time.

I. INTRODUCTION

Key to the successful development of spin-transfer torque magnetic random access memory (STT-MRAM), one of the most promising emerging non-volatile memory technologies today, are new magnetic materials for MTJ memory elements that have sufficient stability against thermal fluctuations to sustain deeply scaled devices. The magnetic electrodes must possess sufficient PMA that their magnetizations lie perpendicular to the plane of the MTJ device, since this allows for reduced currents to switch the magnetization of the electrode that forms the memory layer of the device using spin torque. The most promising magnetic materials to date are considered to be alloys formed from Co, Fe and B, in conjunction with MgO tunnel barriers. Unfortunately, PMA of CoFeB layers arises from the interfaces between these layers and the tunnel barrier and/or underlayer and is too weak to overcome thermal fluctuations when the device has a critical dimension \( \lesssim 20\text{nm} \).

Magnetic materials in which the PMA is derived from volume magnetocrystalline anisotropy (MCA) are then needed. One of the most promising class of such materials are the Heusler alloys - compounds having the chemical formula \( X_2YZ \) wherein X and Y are transition metals, or lanthanides (rare-earth metals), and Z is the main group element. While the parent Heusler compounds are cubic and do not exhibit magnetic anisotropy, the structure of some of these compounds is found to be tetragonally distorted and thus could potentially have large PMA.

Some examples of tetragonal Heusler compounds are \( \text{Mn}_3-\alpha\text{Ga} \) and \( \text{Mn}_3\text{Ge} \). Thin films of these materials have been shown to exhibit large PMA for films grown epitaxially on single crystalline substrates such as \( \text{SrTiO}_3(001) \) or \( \text{MgO}(001) \) and on amorphous substrates (Si(001)/SiO\(_2\)). Unfortunately, the experimental values of the tunneling magnetoresistance (TMR) for MTJs with \( \text{Mn}_3-\alpha\text{Ga} \) or \( \text{Mn}_3\text{Ge} \) electrodes and MgO spacer was found very small, far below the application range.

The goal of present paper is to identify promising tetragonal Heusler compounds that possess PMA and exhibit high TMR either due to large spin polarization of bulk Heusler compound or due to the so-called Brillouin zone (BZ) spin filtering effect for the MTJ with suitable spacer. Realization of the high TMR in a MTJ system with electrodes that have low crystal symmetry where PMA could be simultaneously achieved is of significant technological interest for spintronics applications, and, in particular, in the context of novel STT-MRAM technology that has a potential to become an 'universal memory' combining all the strengths and none of the weaknesses of existing memory types.

II. THEORETICAL SEARCH FOR TETRAGONAL HEUSLER COMPOUNDS WITH PMA AND LARGE TMR

A. Crystal structure

Cubic Heusler compounds \( X_2YZ \) can have regular structure or inverse structure. These two crystal structures are shown in Fig. 1(a) and (c) with four sites forming four fcc sublattices: site Z (occupied by atom Z), site II, octahedrally coordinated by Z, and two equivalent sites I tetrahedrally coordinated by Z. In regular structure shown on Fig 1(a) two X atoms [red, labeled as X(1)] have identical environment - they are located on sites I in the same \( xy \)-plane. In this structure the Y atom (cyan) on site II and Z atom (grey) are located in another \( xy \)-plane. In inverse structure shown on Fig 1(c) two X atoms have different environment - one X atom [red, la-
beled as X(I)] is located on site I in one \( xy \)-plane with 
Y atom (cyan), while another X atom [orange, labeled as 
X(II)] is located on site II in one \( xy \)-plane with Z atom 
(grey).

Regular [Fig 1(b)] and inverse [Fig 1(d)] tetragonal 
Heusler structures can be obtained from regular and 
inverse cubic structures, correspondingly, by stretching 
(or compressing) parent cubic structure along the \( z \)-axis. 
Tetragonal unit cells shown on Fig 1(b) and Fig 1(d) are 
rotated on 45\(^\circ\) around \( z \)-axis relative to the parent cubic 
structures shown on Fig 1(a) and Fig 1(c), correspondingly. 
(Note that only part of atoms from Fig 1(a) and 
Fig 1(c) are shown on Fig 1(b) and Fig 1(d).) Lattice 
constant \( a_{\text{cub}} \) of the cubic Heusler is shown on Fig 1(a) 
and lattice constants \( a \) and \( c \) of the tetragonal Heusler are 
shown on Fig 1(b). For characterization of the tetragonal 
unit cell we use dimensionless parameter \( c' = c/(2a) \) 
that is equal to \( 1/\sqrt{2} \) for the cubic structure, and vary 
between 0.8 and 1.1 for most of the tetragonal Heuslers 
we found (see Table I). Note that for \( c' = 1 \) tetragonal 
structure would become the \( fcc \) structure if all four atoms 
of the compound could be considered as equivalent.

B. Computational details

We performed DFT calculations for both the regular 
and inverse structures (with various magnetic 
configurations) of 286 Heusler compounds\(^\text{15} \) using 
the VASP program\(^\text{16} \) with PAW potentials\(^\text{17,18} \) 
and PBE GGA/DFT functional\(^\text{19} \). In particular, 
we performed calculations for Heusler compounds 
\( X_2YZ \) with \( X = \{ \text{Mn,Fe,Co} \} \) and \( YZ = \{ \text{Mn,Fe,Co,Ni,Cu} \} \{ \text{Al,Be,Co,Ge,Sn,SB} \} \), and \( YZ = \{ \text{Mo,Ru,Rh,Pd,W,Os,Ir,Pt} \} \{ \text{Ga,In,Ge,Sn,SB} \} \), 
\( X = \{ \text{Ru,Rh,Pd} \} \) and \( YZ = \{ \text{Mn,Fe,Co} \} \{ \text{Ga,In,Ge,Sn,SB} \} \), 
\( X = \text{Ni} \) and \( YZ = \{ \text{Mn,Fe,Co} \} \{ \text{Al,Be,Co,Ge,Sn,SB} \} \), \( X = \text{Mn} \) and \( YZ = \{ \text{Fe,Co,Ni,Cu} \} \{ \text{In} \} \), and compounds \( X_3Z \) with 
\( X = \{ \text{Mn,Fe,Co} \} \) and \( Z = \{ \text{In,As} \} \). For binary compounds 
\( X_3Z \) we also considered hexagonal structures 
with \( X \) atoms forming a Kagome lattice in a plane with 
a \( Z \) atom in the center of the hexagon (see, e.g., Ref\(^\text{20} \)
for figure of the hexagonal structure).

The results of calculations are summarized in Table I 
for 116 compounds with tetragonal lowest energy config-
uration and \( E_{21} \geq 0.05 \text{ eV} \), where phase stability energy, 
\( E_{21} \), is defined as the difference between the total energy 
of the second lowest energy configuration and the total 
energy of the lowest energy configuration. The remaining 
170 compounds that are not included in Table I ether have 
cubic or hexagonal lowest energy configuration or tetrag-
onal lowest energy configuration with low phase stability 
energy, \( E_{21} < 0.05 \text{ eV} \). (See Ref.\(^\text{15} \) for explanation of such 
a large share of stable tetragonal compounds - 116 - out of 
286 studied compounds.) The convergence of presented 
results was verified by varying the number of divisions in 
reciprocal space from \( 10 \times 10 \times 10 \) to \( 18 \times 18 \times 18 \) and 
the energy cut-off from 400eV to 520eV.

The MCA energy, \( K_{mc} \), of tetragonal Heusler com-
ounds is calculated as the difference between total en-
ergies of states with magnetization along the \( x \)-axis and 
the \( z \)-axis, \( K_{mc} = E_{(100)} - E_{(001)} \), where positive \( K_{mc} \) 
means out-of-plane magnetization. We also calculated 
the volume magnetic anisotropy, \( K_v = K_{mc} - K_{zh} \), where \( K_{zh} = \mu_0 M_s^2 V/2 \), is the shape anisotropy energy of thin 
film per unit cell of volume \( V \), and \( M_s \) is saturation mag-
etisation and \( \mu_0 \) is vacuum permeability.

We calculated Curie temperature, \( T_C \), within the stan-
ard mean-field approximation (MFA)\(^\text{21} \) using the ex-
change constants, \( J_{ij} \), of the effective Heisenberg Hamil-
tonian (\( i \) and \( j \) are the site indexes). In this approach 
\( T_C \) can be estimated as \( k_B T_C = 2/3J_{max} \), where \( J_{max} \) is 
the maximal eigenvalue of the \( (4 \times 4) \) \( J_{\mu\nu} \) matrix, with 
\( J_{\mu\nu} = \sum_{j \in \nu} J_{0j} \). Here \( 0 \) is fixed index in sublattice \( \mu \) 
and sum is taken over sites in sublattice \( \nu \). The exchange 
constants \( J_{ij} \) were calculated by using the Green’s 
function approach implemented within the LMTO-ASA 
framework\(^\text{22,23} \).

For each stable tetragonal compound Table I shows the 
lattice parameters \( a \) and \( c' \), the lowest and the second 
lowest energy configurations labels \( s_1 \) and \( s_2 \), magnetic 
moment \( m \), phase stability energy \( E_{21} \), total spin po-
larization \( SP_1 \) as well as the spin polarization of individ-
ual termination layers \( SP_1 \) and \( SP_2 \), anisotropy constants
<table>
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<th>Alloys</th>
<th>$a$</th>
<th>$c$</th>
<th>$s_1$</th>
<th>$s_2$</th>
<th>$e_1^m$</th>
<th>$e_2^m$</th>
<th>$K_{mc}$</th>
<th>$K_{sh}$</th>
<th>$K_{v}$</th>
<th>$T_C$</th>
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<td>0.88</td>
<td>0.06</td>
<td>1.01</td>
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<td>0.16</td>
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<td>0.14</td>
<td>0.00</td>
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TABLE I: Calculated lattice parameters, $a$, and $c$, labels of the lowest energy configuration, $s_1$, and the second lowest energy configuration, $s_2$, the phase stability energy, $E_1^m$, magnetic moment, $m$, total spin polarization, $SP_1$, spin polarizations, $SP_2$, and $SP_3$, of two termination layers, anisotropy constants, $K_{mc}$, $K_{sh}$, and $K_v$, and the Curie temperature, $T_C$, for 116 stable tetragonal Heuslers with $E_2^m \geq 0.05eV$ (see text for details).

$K_{mc}$, $K_{sh}$, and $K_v$ and $T_C$. For ternary compounds labels $s_1, s_2 = tr, ti, cr$, or $ci$ represent tetragonal regular, tetragonal inverse, cubic regular, or cubic inverse phase, correspondingly. For binary compounds $s_1, s_2 = t, c$, or $h$ represent tetragonal, cubic or hexagonal phase, correspondingly. Since only stable tetragonal compounds are presented in Table I, $s_1$ always indicates tetragonal phase, $s_2 = tr, ti, cr$, or $ci$. Anisotropy constants $K_{mc}$ and $K_{sh}$ are shown in Table I in $\text{meV/Å}^2$ units, while $K_v$ is converted from $\text{meV/Å}^2$ to $\text{meV}$ units. Positive $K_v$ indicates that this compound has PMA. Three values of the spin polarisation shown in Table I - $SP_1$, $SP_2$, and $SP_3$ - are defined as $\text{DOS}^+ - \text{DOS}^-$, where $\text{DOS}_1$, $\text{DOS}_2$, and $\text{DOS}_3$ are density of states at the Fermi energy, $E_F$, of majority, minority electrons at $E_F$.
calculated for the whole system, projected to two-atom termination layer (xy-plane), which does not contains atom Z, or to two-atom termination layer that contains atom Z, correspondingly.

C. Compounds with expected large TMR due to Brillouin zone spin filtering effect

The so-called Brillouin zone (BZ) spin filtering effect\(^1\) in a ME/MgO/ME MTJ system occurs if magnetic electrode (ME) has states at the Fermi energy, \(E_F\), along the \(\Gamma-Z\) line in one spin channel, \(\sigma_1\), and does not have such states in another spin channel, \(\sigma_2\). [\(\Gamma-Z\) line in BZ is the line along \(k_z\) direction with in-plane wavevector \(k_{||} = (k_x, k_y) = 0\).] It is well known\(^{24,25}\) that the smallest (at given \(k_{||}\)) attenuation constant \(\gamma(k_{||})\) of MgO for evanescent states propagating along the \(z\)-direction with energies within the MgO band gap reaches a minimum \(\gamma_{\text{min}}\) at \(k_{||} = 0\). When \(k_{||}\) increases, \(\gamma(k_{||})\) increases as \(\gamma(k_{||}) = \gamma_0 + \alpha k_{||}^2\) (with \(\alpha > 0\)). Therefore, at \(E = E_F\), the evanescent states of ME in \(\sigma_1\) spin channel that propagate along \(z\) direction with \(k_{||} = 0\) will decay inside MgO as \(e^{-\gamma_{\text{min}} z}\), whereas evanescent states in \(\sigma_2\) spin channel will decay as \(e^{-\gamma(z + \alpha k_{||}^2) z}\), with \(|k_{||}| > 0\) since \(\sigma_2\) channel does not have states at \(E_F\) with \(k_{||} = 0\). As a result the TMR increases exponentially with increasing MgO thickness, \(d_{MGO}\): 

\[
\text{TMR} \propto \exp(2\alpha k_{||}^2 d_{MGO}),
\]

where \(k_{||}\) is the shortest vector \(k_{||}\) for which ME has states in the \(\sigma_2\) spin channel at \(E_F\). Such dependence on \(d_{MGO}\) is much stronger than the \(TMR \propto d_{MGO}^n\) dependence arising from the symmetry filtering effect\(^{24,25}\), where the power factor \(n\) can only take three values \(n = 0, 1, 2\) for MTJ systems with square symmetry in \(xy\) plane\(^2\).

Table II shows the values of \(E_z = E_c - E_F\) for 26 compounds that have band gap along \(\Gamma-Z\) line (\(|E_z| > 0\)) in only one spin channel, and for FeCoCuAl and FeCuGa that have band gap (\(|E_z| > 0\)) in both spin channels. Here \(E_c\) is the closest to \(E_F\) energy among energies of states in corresponding spin channel with \(k\) along the \(\Gamma-Z\) line. The value of \(|E_z|\) characterizes the strength of the BZ filtering effect since larger \(|E_z|\) leads to larger value of \(k_{||}\) and, therefore, to faster TMR increase with \(d_{MGO}\). Also, large values of \(|E_z|\) make the existence of the BZ filtering effect less susceptible to the details of calculations (choice of the DFT functional, variations of the lattice constants, etc) as well as to the experimental conditions (effects of disorder, finite temperature, finite applied bias, etc).

The majority (minority) spin channel with \(|E_z| > 0\) is indicated in Table II by an up (down) arrow. Positive (negative) \(E_z\) indicates that the band closest to \(E_F\) is located above (below) \(E_F\). For each compound \(E_z\) was calculated by three different methods: the pseudo-potential PAW approach implemented in VASP program with PBE GGA/DFT functional, the full-potential all-electron LMTO approach\(^27\) with Barth-Hedin LDA/DFT functional\(^28\), and the QSGW method that is known to describe band gaps and other properties of materials with moderate e-e correlations significantly better than DFT\(^{29-31}\). Three values of \(E_z\) are indicated as \(E_{z}^{\text{GGA}}, E_{z}^{\text{LDA}},\) and \(E_{z}^{\text{QSGW}},\) correspondingly in Table II. The majority and minority bands along the \(\Gamma-Z\) line calculated by the GGA/DFT, LDA/DFT, and QSGW methods are shown for 28 compounds in Figs. 2-5 by red, green, and blue colors, correspondingly.

Table II shows that for MnSnCuSn, FeZCoGa, and FeCuMoSb compounds \(|E_z^{\text{GGA}}| > 0\) and \(|E_z^{\text{LDA}}| > 0\), while the gap along \(\Gamma-Z\) closes in QSGW, \(|E_z^{\text{QSGW}}| = 0\). On the other hand for NiZCoGe, CoZSnNi, and CoPdG Ga compounds \(|E_z^{\text{QSGW}}| = |E_z^{\text{LDA}}| = 0\), while the gap along \(\Gamma-Z\) line opens in QSGW, \(|E_z^{\text{QSGW}}| > 0\). Thus, beyond DFT calculations are necessary in order to accurately estimate \(E_z\). Note that for one of the most studied tetragonal Heusler compound, MnSnGe, the QSGW value \(|E_z^{\text{QSGW}}| = 0.03\)eV is significantly smaller than Ga value \(|E_z^{\text{GGA}}| = 0.08\)eV. Therefore, high TMR values predicted previously by DFT calculations in MnSnGe/MgO/MnSnGe MTJs\(^12,32\) are expected to be significantly lower if calculated by more accurate beyond DFT methods.

Table II shows that there are 17 compounds with relatively large \(|E_z^{\text{QSGW}}| > 0.15\)eV. These compounds are expected to exhibit large TMR in MTJ devices. Among these 17 compounds 13 have PMA (\(K_s > 0\)) and 10 have strong PMA with \(K_s > 0.5M_J/m^3\): MnSn, MnSb, MnCuSi, MnCuGe, MnOsGe, FeCoSn, FeCoNiSn, FePdGe, FePtGe, and FePtSi. These 10 compounds constitute our ‘best’ candidates for STT-MRAM applications identified in present paper. Note, that five Fe-based compounds in this list have high \(T_C > 1000K\) (see Table I).

D. Compounds with expected large TMR due to large spin polarization

Large spin polarization of bulk Heusler compound also could result in enhanced TMR values. We identified
FIG. 2: Majority (↑) and minority (↓) bands of Mn$_2$Ge, Mn$_2$Sn, Mn$_2$Sb, Mn$_2$CoSn, Mn$_2$NiSi, Mn$_2$NiGe, and Mn$_2$CuSi along the Γ-Z line. GGA, LDA, and QSGW bands are shown by the red, green, and blue colors. Vertical scale is $E - E_F$ (eV).

FIG. 3: Majority (↑) and minority (↓) bands of Mn$_2$CuGe, Mn$_2$CuSn, Mn$_2$MoSn, Mn$_2$MoSb, Mn$_2$WSb, Mn$_2$OsGe, and Mn$_2$CoGe along the Γ-Z line. GGA, LDA, and QSGW bands are shown by the red, green, and blue colors. Vertical scale is $E - E_F$ (eV).

11 compounds - Mn$_3$In, Mn$_2$FeIn, Mn$_3$Ge, Mn$_2$CoGe, Mn$_3$Sn, Mn$_2$CoSn, Mn$_2$RuSn, Mn$_2$IrIn, Mn$_2$OsGe, Mn$_2$OsSn, and Pd$_2$CoS - in Table I that have large total spin polarization, $|S_P| > 0.7$ and, simultaneously, PMA with $K_v > 0.6MJ/m^3$. These 11 compounds constitute our ‘second best’ list of candidates for STT-MRAM applications. Eight compounds from this list have very strong PMA with $K_v \geq 1.8MJ/m^3$ and nine compounds have $T_C > 460K$. Note that the sign of the spin polarization is the same for both termination layers for these 11 com-
FIG. 4: Majority (↑) and minority (↓) bands of Fe₂MnSn, Fe₂NiSi, Fe₂NiGe, Fe₂NiSn, Fe₂NiSb, Fe₂CuAl, and Fe₂CuGa along the Γ-Z line. GGA, LDA, and QSGW bands are shown by the red, green, and blue colors. Vertical scale is $E - E_F$ (eV).

FIG. 5: Majority (↑) and minority (↓) bands of Fe₂MoSb, Fe₂PdGe, Fe₂PdSb, Fe₂PtGe, Fe₂PtSb, Co₂NiGa, and Co₂PdGa along the Γ-Z line. GGA, LDA, and QSGW bands are shown by the red, green, and blue colors. Vertical scale is $E - E_F$ (eV).

Compounds (see Table I) which is important since, as was discussed in Ref. 12, in real devices both terminations can be randomly realized at the ME/MgO interface. If the signs of $S_{P_1}$ and $S_{P_2}$ were different, the spin polarization of the tunneling current in areas with different terminations would have different sign, thereby reducing total TMR.

Two Heusler compounds - Mn₃Sn and Mn₂OsGe - belong to both lists since they simultaneously have large spin polarization and BZ filtering conditions. Unfortunately, both effects tend to cancel each other for these
TABLE III: The experimental \((c^s, m^s, K^s_{/0})\) and calculated \((c^{th}, m^{th}, K^{th}_{/0})\) values of the lattice constant, \(c\), magnetic moment, \(m\), and anisotropy constant, \(K_v\), for 17 measured Heusler compounds. \(s^s\) and \(s^{th}\) label experimentally found and the lowest-energy DFT-calculated structures (except for Fe\(_2\)MnGa where DFT results are shown for tetragonal phase that is 0.03 eV higher in energy than cubic one). The symbol "\(\Delta\)" in some of experimental \(K^s_{/0}\) means that shown value is a lower bound for \(K^s_{/0}\).

<table>
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<tr>
<th>Compound</th>
<th>(s^s) (c^s) (m^s) (K^s_{/0})</th>
<th>(s^{th}) (c^{th}) (m^{th}) (K^{th}_{/0})</th>
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<tr>
<td>(\text{MgO(001)/Cr/Ir} ) &amp; 7 &amp; 140 &gt; 0.45 tet 7.09 190 2.40</td>
<td></td>
<td></td>
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<tr>
<td>(\text{MgO(001)/Cr/IrMn}_3) &amp; 7 &amp; 160 &gt; 0.52 tet 7.47 167 2.65</td>
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<tr>
<td>(\text{MgO(001)/Cr/IrMn}_3) &amp; 7 &amp; 300 &gt; 1.05 tet 7.23 158 1.59</td>
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<tr>
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<td>(\text{MgO(001)/Cr/IrMn}_3) &amp; 6 &amp; 120 &gt; 0.06 tet 7.80 870 2.18</td>
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</tr>
<tr>
<td>(\text{MgO(001)/Cr/IrMn}_3) &amp; 7 &amp; 175 &gt; 0.06 tet 7.70 0 1.44</td>
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</table>

For small \(d_{\text{MgO}}\) (when effect of BZ filtering is small) the tunneling (inside MgO barrier) spin polarization for these compounds is expected to be dominated by the spin polarization of bulk Heuslers and have negative sign, while for large \(d_{\text{MgO}}\) the sign of the tunneling spin polarization should switch to positive due to increasing role of the BZ filtering effect.

We note that for ideal junctions the candidate materials from the 'best' list should have high priority for experimental study as compared to the materials from the 'second best' list since TMR should grow exponentially with the BZ filtering effect. The 'second best' list is not expected to vary much when \(d_{\text{MgO}}\) increases. On the other hand, the BZ filtering effect relies on existence of a well-defined surface Brillouin zone and in real devices (with lattice mismatch and disorder) the TMR enhancement due to the BZ filtering effect could be suppressed. The spin polarization induced enhancement of the TMR for MTJs with electrodes from the 'second best' list is not expected to vary much when \(d_{\text{MgO}}\) increases. On the other hand, the BZ filtering effect relies on existence of a well-defined surface Brillouin zone and in real devices (with lattice mismatch and disorder) the TMR enhancement due to the BZ filtering effect could be suppressed. The spin polarization induced enhancement of the TMR is less sensitive to the disorder and lattice mismatch. Therefore, both the 'best' list and the 'second best' list of candidate materials should be experimentally explored since the winner material could belong to any of these lists.

III. EXPERIMENTAL IDENTIFICATION OF TETRAGONAL HEUSLER COMPOUNDS WITH PERPENDICULAR MAGNETIC ANISOTROPY

We performed experimental measurements for 32 Heusler compounds. 20-30 nm thick films of these Heusler compounds were prepared by either dc-magnetron sputtering or ion-beam deposition in an ultra-high vacuum chamber (base pressure \(4 \times 10^{-10}\) Torr). Various buffer layers of Si/SiO\(_2\)/TaN/IrM\(_3\), Si/SiO\(_2\)/TaN/IrM\(_3\)/TaN, MgO(001) MgO(001)/Cr, MgO(001)/Cr/Ir, MgO(001)/Cr/IrMn\(_3\) were used to reduce lattice mismatch between Heusler compounds and the substrate. Each Heusler compound was grown at several different substrate temperature, typically 100°C - 600°C, and magnetic properties of them were measured by Quantum Design superconducting quantum interference device vibrating sample magnetometer (SQUID-VSM) in magnetic fields of up to \(\pm 7\) T. More details on the experimental set-up can be found in\(^{12}\).

Comparison of the experimental results with theoretical predictions for 17 compounds are presented in Table III. Experimental measurements confirm the existence of tetragonal phase for 10 compounds that are predicted to be tetragonal and stable cubic phase for 6 compounds that are predicted to be cubic. Fe\(_2\)MnGa was found to be tetragonal in experiment, while predicted to be 'unstable' cubic in theory (tetragonal phase of Fe\(_2\)MnGa is only 0.03 eV higher in energy than cubic phase\(^{15}\)). Note that 9 out of 11 tetragonal compounds in Table III have PMA in both the experiment and theory (exceptions are Mn\(_2\)WSb and Rh\(_2\)CoSb where \(K^v_{/0} < 0\), but \(K^{th}_{/0} > 0\)).

Remaining 15 out of 32 measured compounds include Co\(_2\)NiGe, Co\(_2\)RhSb, Mn\(_2\)NiSb, Mn\(_2\)CuSn, Fe\(_2\)CuAl, Co\(_3\)Sb, Co\(_3\)Ge, Fe\(_2\)CuSb, Mn\(_2\)CuS\(_3\), Co\(_2\)IrSb, Ru\(_2\)CoGa, Mn\(_2\)PtSb, Fe\(_2\)PtSb, Mn\(_2\)OsS\(_3\). All these compounds were predicted to have tetragonal phase by DFT calculations but were found to be cubic in experiment. We attribute this discrepancy to the effects of disorder that favour high-symmetry cubic phase. Since DFT calculations assume zero temperature, the finite temperature effects could also contribute to this discrepancy.

Despite disagreement between theoretical predictions and experimental results for some studied compounds, experimental confirmation of tetragonality for 10 out of 26 measured compounds that were predicted to be tetragonal by the theory shows that DFT calculations for ideal systems (without taking into account disorder and finite temperature effects) can still correctly predict tetragonally in significant share of studied cases. Moreover, for majority of found tetragonal compounds (9 out of 11) theory also correctly predicted PMA.

IV. CONCLUSION

In conclusion, we performed DFT calculation for 286 Heuslers in cubic, tetragonal and hexagonal phases, and identified 116 stable tetragonal compounds. Out of these 116 materials we identified 19 potential candidates for electrodes for STT-MRAM MTJ devices. These 19 compounds simultaneously have PMA (with high \(K^v_{> 0.9M_J/m^3}\) for 15 of these materials) and expected to have...
enhanced TMR ether due to the strong BZ filtering effect ($|E_z| > 0.15\text{eV}$) or due to the high spin polarization ($|SP| > 0.7$). The QSGW calculations of the band structure preformed for 28 stable tetragonal compounds that satisfy the BZ filtering conditions show that beyond DFT methods are needed to accurately evaluate the strength (and even existence) of the BZ filtering effect.

We performed experimental measurements for 32 Heusler compounds. To the best of our knowledge majority of the tetragonal compounds presented in Table III are experimentally identified as tetragonal compound with PMA for the first time (exceptions are known tetragonal compounds Mn$_3$Ge$^7$, Mn$_2$FeGa and Fe$_2$MnGa$^{33}$). Our experimental results show that DFT calculations can correctly predict both tetragonally and PMA in significant share of studied cases. Therefore, one can expect that experimental measurements for Heusler compounds theoretically predicted to be tetragonal with PMA in the present work (as well as in further theoretical studies) will result in experimental identification of significant number of stable tetragonal Heusler compounds with PMA suitable for spintronics applications.

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