Electronic structure and magnetic properties in $T_2\text{AlB}_2$ ($T = \text{Fe, Mn, Cr, Co, and Ni}$) and their alloys

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The electronic structure and intrinsic magnetic properties of Fe$_2$AlB$_2$-related compounds and their alloys have been investigated using density functional theory. For Fe$_2$AlB$_2$, the crystallographic $a$ axis is the easiest axis, which agrees with experiments. The magnetic ground state of Mn$_2$AlB$_2$ is found to be ferromagnetic in the basal $ab$ plane, but antiferromagnetic along the $c$ axis. All 3$d$ dopings considered decrease the magnetization and Curie temperature in Fe$_2$AlB$_2$. Electron doping with Co or Ni has a stronger effect on the decreasing of Curie temperature in Fe$_2$AlB$_2$ than hole doping with Mn or Cr. However, a larger amount of Mn doping on Fe$_2$AlB$_2$ promotes the ferromagnetic to antiferromagnetic transition. A very anisotropic magnetoelastic effect is found in Fe$_2$AlB$_2$: the magnetization has a much stronger dependence on the lattice parameter $c$ than on $a$ or $b$, which is explained by electronic-structure features near the Fermi level. Dopings of other elements on B and Al sites are also discussed.

I. INTRODUCTION

Magnetic cooling, which is based on the magnetocaloric effect (MCE) and was discovered one century ago, has long been used in scientific laboratories to attain extremely low temperatures. A major breakthrough came in the late 1990s when Pecharsky and Gschneidner discovered giant MCE around room temperature (RT) [2]. The reported entropy change has a value of $\Delta S_m = 4.1$–7.7 $\text{J kg}^{-1} \text{K}^{-1}$ in the presence of an external field $B = 2$–5 T. Although Fe$_2$AlB$_2$ does not have the largest MCE of all materials, it does not contain any rare, expensive, or toxic elements. Moreover, its volume barely changes during the magnetic transition [3], which may ensure Fe$_2$AlB$_2$ has a good life span for refrigerator applications operating at high cycle frequencies [4, 5].

The MCE often peaks at the Curie temperature $T_C$ of the material; however, real applications require materials with a large MCE over a certain operating temperature range. This likely needs to be achieved by using composite materials with multiple compositions, so the system can have MCE over the whole operating temperature range for specific applications. It seems the first logical selection of doping would be the substitution of Fe with other 3$d$ transition-metal elements $T$. Pure Mn$_2$AlB$_2$ [6] and Cr$_2$AlB$_2$ [7] can be formed and share the same structure of Fe$_2$AlB$_2$. Combining theory with experiments, Kádas et al. studied the phase stability in $T_2\text{AlB}_2$ with $T = \text{Cr, Mn, Fe, Co, and Ni}$. They found that although compounds are metastable with $T = \text{Co and Ni}$, Fe$_{2-x}\text{Co}_x\text{AlB}_2$, Fe$_{2-x}\text{Ni}_x\text{AlB}_2$, or even (Fe$_{2-x}\text{Co}_y\text{Ni}_y$)AlB$_2$ could be stable [8]. However, the magnetic properties of those alloys or even their parent compounds are not well understood. For example, the magnetic ground state of Mn$_2$AlB$_2$ had been reported to be ferromagnetic (FM) [6], but recent experiments concluded that it should be either nonmagnetic (NM) or antiferromagnetic (AFM) [9]. To provide guidance on tuning Fe$_2$AlB$_2$, a better understanding of the magnetic properties of pure $T_2\text{AlB}_2$ and their alloys is desired.

The high melting temperature of FeB makes it a difficult impurity to remove from Fe$_2$AlB$_2$ samples. The rapid cooling by melt spinning had been used to greatly improve the Fe$_2$AlB$_2$ purity by suppressing the growth of FeB [4]. On the other hand, extra Al is often added during the synthesis to decrease the formation of FeB impurities [4, 10]. With a higher Al content, Al$_{13}\text{Fe}_4$ becomes the main impurity phase. Reported magnetization values measured at low temperature vary between 1.0 and 1.32 $\mu_B$/Fe and the $T_C$ values vary between 282 and 320 K [2, 4, 9, 11]. The variation of experimental values may be due to the existence of an impurity phase in the Fe$_2$AlB$_2$ sample.

Experimentally, substitution of Mn [4, 5, 9] or up to 15% of Co [10] on Fe sites had been reported; a large amount of Mn or Co doping makes the structures unstable [4] or phase inhomogeneous [9]. Both dopings decrease the magnetization and $T_C$ in Fe$_2$AlB$_2$. A spin-glass state had been found in Fe$_{1.5}$Mn$_{0.5}$AlB$_2$ at low temperature [5]. With Co doping, $T_C$ and the Co content are

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Electronic structure and most magnetic properties are calculated using a standard linear muffin-tin orbital (LMTO) basis set [15] generalized to full potentials (FP) [16]. This scheme employs generalized Hankel functions as the envelope functions. Calculations are carried out within the generalized gradient approximation (GGA) to DFT with the exchange-correlation parametrization of Perdew, Burke, and Ernzerhof (PBE) [17], unless LDA [18] (local density approximation, with the exchange-correlation parametrization of von Barth and Hedin) is specified.

The magnetocristalline anisotropy energy (MAE) is calculated using the force theorem [19]. Starting from the self-consistent scalar-relativistic potential, the spin-orbit coupling (SOC) is included in a subsequent one-step calculation with spin being along direction \( \hat{n} \). The MAE is characterized below as

\[
S_{\text{MAE}} = E_{\text{MAE}} - E_{\text{MAE}}^{001},
\]

where \( E_{\text{MAE}}^{001} \) and \( E_{\text{MAE}} \) are the summation of occupied band energies for the magnetization being oriented along the [001] and \( \hat{n} \) directions, respectively.

Exchange coupling parameters \( J_{ij} \) are calculated using a static linear-response approach implemented in a Green’s function (GF) LMTO method, simplified using the atomic sphere approximation (ASA) to the potential and density [20][21]. The scalar-relativistic Hamiltonian is used so SOC is not included, although it is a small perturbation on \( J_{ij} \)’s. In the basis set, \( s,p,d \) orbitals are included for \( T \) and Al atoms, and \( s,p \) orbitals are included for the B atom. A dense \( k \)-point mesh is used to calculate exchange parameters \( J(q) \), e.g., a \( 32^3 \) \( k \)-point mesh for the five-atom cell. The real-space \( J(R) \) are obtained by a subsequent Fourier transform. Curie temperatures are estimated in the mean-field approximation (MFA) with \( k_B T_C = 2/3 \sum_i n_i J_i \). The coherent potential approximation (CPA) implemented within the LMTO-ASA-GF code is used to address the chemical effects of doping on magnetization and \( T_C \). Without using supercell calculations, the CPA provides an elegant and efficient approach to investigate substitutional effects with an arbitrary composition. The details of the methods and applications can be found elsewhere [21][22].

Both experimental and theoretically optimized crystal structures are used to investigate the magnetic properties. We fully relax internal atomic positions and lattice constants with the PBE functional using a fast
plane-wave method, as implemented within the Vienna *ab initio* simulation package (VASP) [23][24]. The nuclei and core electrons are described by the projector augmented-wave potential [25] and the wave functions of valence electrons are expanded in a plane-wave basis set with a cutoff energy of up to 520 eV.

### III. RESULTS AND DISCUSSION

#### A. Pure compounds: Exchange coupling, magnetic anisotropy, and spin configurations

Table I shows the atomic spin moments $m_i$ at each sublattice and magnetization $M$ in Fe$_2$AlB$_2$, which are calculated using the experimental lattice constants and atomic position parameters from Ref. [26]. Al and B have small moments antiparallel to the Fe sublattice. Within the GGA, a magnetization of $M = 1.36 \mu_B$/Fe is obtained using FP. For the sake of comparison, we carry out similar calculation for the parent compound, FeB, and obtain a magnetization of $M = 1.20 \mu_B$/Fe. The smaller Fe moment in FeB is likely due to its smaller Fe-Fe bond length (2.62 Å) than in Fe$_2$AlB$_2$. ASA gives a slightly smaller (by 4%) magnetization than FP in Fe$_2$AlB$_2$, suggesting that ASA is suitable for this material. The calculated $T_C = 329$ K is slightly above the upper bound of the reported experimental $T_C$ values. The agreement is fair considering the MFA generally overestimates $T_C$. LDA gives smaller magnetization, especially with ASA, resulting in a smaller $T_C$.

Starting from the FM configuration and using experimental crystal structures, we calculate the exchange coupling $J_{ij}$ in Fe$_2$AlB$_2$ and Mn$_2$AlB$_2$. Figure 2 shows the $J_{ij}$ as a function of the distance $R_{ij}$. In both compounds $J_{ij}$ becomes negligible after $R_{ij} > 6$ Å. The exchange parameters between the first few nearest neighbors are also listed in Table I. Here, $J_{ij}$ can be treated as stability parameters and a negative $J_{ij}$ indicates that the given spin configuration is not favorable for that particular pair of sites [21].

For Fe$_2$AlB$_2$, all of the first four nearest exchange parameters are positive. The $J_{ij}$ value increases with distance, reaching maximum at $J_b$, and then decrease, which generally agrees with the previous study [13]. LDA gives a similar trend but a smaller amplitude of $J_{ij}$ than GGA, which reflects the smaller magnetic moments obtained within LDA.

The magnetic ground state of Mn$_2$AlB$_2$ is not well understood [9]. For simplicity, we start from the FM configuration. The calculated magnetization is 0.42 $\mu_B$/Mn, which agrees well with a previous FM calculation [9]. Exchange parameters calculated in the FM configuration show a very interesting feature: all dominant $J_{ij}$ are positive for neighbors within the Mn $ab$ plane but negative for neighbors between neighboring Mn layers, namely, $J_c$, $J_{abc}$, $J_{ac}$, and $J_{bc}$. This suggests that the FM coupling of Mn atoms is stable within the $ab$ layer but not between neighboring layers. To confirm it, we calculate $J_{ij}$ for the AFM configuration, in which FM Mn $ab$ layers couple antiferromagnetically along the $c$ axis. This AFM configuration gives lower energy than the FM configuration. Moreover, as shown in Fig. 2(b), the dominant exchange parameters become all positive and larger. To better quantify the relative stability of those two spin configurations, we fully relaxed the structure and found that the AFM configuration increases the on-site Mn moment to 0.75 $\mu_B$/Mn and lowers the total energy by 42 meV/f.u. Unlike Fe$_2$AlB$_2$, the largest exchange interaction in Mn$_2$AlB$_2$ is $J_{ab}$, which is between...

### Table I. Calculated atomic spin magnetic $m_i$, spin magnetization $M$, and Curie temperature $T_C$ in Fe$_2$AlB$_2$.

|          | Fe   | Al   | B    | $m_i$ ($\mu_B$/atom) | $M$ ($\mu_B$/f.u.) | $T_C$ (K) |
|----------|------|------|------|----------------------|-------------------|---------|
| FP-GGA   | 1.43 | -0.04| -0.01| 2.73                 |                   |         |
| ASA-GGA  | 1.38 | -0.08| -0.04| 2.62                 | 329               |         |
| FP-LDA   | 1.31 | -0.01| -0.03| 2.54                 |                   |         |
| ASA-LDA  | 1.20 | -0.06| -0.03| 2.29                 | 232               |         |

#### FIG. 2. Real-space magnetic exchange parameters $J_{ij}$ in Fe$_2$AlB$_2$ (a) and Mn$_2$AlB$_2$ (b) as functions of distance. For Fe$_2$AlB$_2$, both GGA and LDA results are shown. For Mn$_2$AlB$_2$, both FM and AFM spin configurations are calculated within GGA. The spin configurations of their magnetic ground states are shown in the insets.
the nearest Mn neighbors. The Néel temperature is estimated to be \( T_N = 310 \text{ K} \) within MFA for the AFM configuration with the experimental crystal structure.

Next we consider the SOC effect in Fe\(_2\)AlB\(_2\). Figure 3 shows the energy and the average orbital magnetic moments of each sublattice as functions of spin quantization axis orientation, which rotates from the \( c \rightarrow a \rightarrow b \rightarrow c \) axis. The relaxed structure was used for the calculations.

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**TABLE II. Pairwise exchange parameters** \( J_{ij} \) for the Heisenberg Hamiltonian \( H = -\sum J_{ij} \hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_j \), and \( \hat{\mathbf{e}}_i \) is the unit vector pointing along the direction of the local spin moment at site \( i \). The experimental lattice parameters and atomic positions are used. For Fe\(_2\)AlB\(_2\), both GGA and LDA results are shown. For Mn\(_2\)AlB\(_2\), the PBE functional is used, and both FM and AFM spin configurations are considered.

| Lbl. | No. | \( R_{ij} \) (Å) | \( R_{ij} \) (a) | \( x \) | \( y \) | \( z \) | \( J_{ij} \) (meV) |
|------|-----|------------------|------------------|-----|-----|-----|--------------|
| \( J_{ab} \) | 2 | 2.721 | 0.931 | 0.5 | 0.785 | 0 | 2.95 | 1.41 |
| \( J_c \) | 2 | 2.870 | 0.982 | 0 | 0 | 0.982 | 7.36 | 4.29 |
| \( J_b \) | 2 | 2.923 | 1 | 1 | 0 | 0 | 14.58 | 10.63 |
| \( J_b \) | 1 | 3.222 | 1.102 | 0 | 1.102 | 0 | 25.41 | 20.37 |
| \( J_{abc} \) | 4 | 3.955 | 1.353 | 0.5 | -0.785 | 0.982 | -0.43 | 0.01 |
| \( J_{ac} \) | 4 | 4.097 | 1.401 | 1 | 0 | 0.982 | -2.76 | -1.49 |
| \( J_{bc} \) | 2 | 4.315 | 1.476 | 0 | 1.102 | 0.982 | -2.63 | -2.37 |
| \( J'_{ab} \) | 2 | 4.350 | 1.488 | 1 | 1.102 | 0 | -4.62 | -4.62 |
| \( J'_{ab} \) | 2 | 4.949 | 1.693 | 1.5 | -0.785 | 0 | -2.03 | -1.43 |

For Fe\(_2\)AlB\(_2\), both GGA and LDA results are shown. For Mn\(_2\)AlB\(_2\), the PBE functional is used, and both FM and AFM spin configurations are considered.

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Next we consider the SOC effect in Fe\(_2\)AlB\(_2\). Figure 3 shows the energy and the average orbital magnetic moments of each sublattice as functions of spin quantization axis orientation, which rotates from the \( c \rightarrow a \rightarrow b \rightarrow c \) axis. The relaxed structure was used for the calculations. The \( a \) axis is the easiest axis, which agrees with recent neutron scattering experiments [13]. The \( c \) axis is the hardest axis, while the anisotropy within the \( ab \) plane is very small. Energy changes by \( K_{100} = -0.38 \text{ meV/f.u.} \) (\(-1.34 \text{ MJ/m}^3\)) when the spin quantization axis rotates from the \( c \) axis to the \( a \) axis. The anisotropy calculated using experimental structure [26] is larger by \(-10%\), reaching \( K_{100} = -1.47 \text{ MJ/m}^3\). B and Al atoms have negligible orbital magnetic moments, as expected for light \( 2p \) and \( 3p \) elements. The orbital moment of Fe is also rather small, and interestingly has the largest value of \( 0.02 \mu_B/\text{Fe} \) when spin is along the hardest \( c \) axis instead of in the \( ab \) plane. Similar behavior has also been found in materials such as FePt [27]. To elucidate the origin of MAE, we evaluate the anisotropy of the on-site SOC energy with respect to the \( c \) axis and the \( ab \) plane, \( K_{110}^{so} = \frac{1}{22}V_{so/110} - \frac{1}{22}V_{so/001} \), and resolve it into four spin channels [28, 29]. It is well known that only when the MAE is dominated by the \( \downarrow \downarrow \) term, one may expect an obvious correlation between the orbital moment and MAE, and a larger orbital moment along the easy axis [28, 30]. As shown in the inset of Fig. 3(b), the amplitudes of four spin components of \( K_{so}^{2σ′} \) are comparable. The \( \downarrow \downarrow \) term favors the spin to be along the \( c \) axis, while the other three terms (\( \uparrow \uparrow, \downarrow \downarrow \), and \( \downarrow \uparrow \)) favor the spin to lie in the \( ab \) plane, explaining the absence of the correlation between MAE and orbital moment in Fe\(_2\)AlB\(_2\). LDA gives a smaller anisotropy (\( K_{100} = -0.82 \text{ MJ/m}^3 \) using experimental structure) but a similar trend of angular dependence of energy. For Mn\(_2\)AlB\(_2\), the \( c \) axis is also the hardest axis. Within the \( ab \) plane, the system has slightly lower energy when the spin is along the \( b \) axis. As expected, its anisotropy is much smaller than in Fe\(_2\)AlB\(_2\). The schematic representation of the ground-state spin configurations of Fe\(_2\)AlB\(_2\) and Mn\(_2\)AlB\(_2\) are shown in the insets of Fig. 2.

Figure 4 shows the scalar-relativistic partial density of states (PDOS) projected on individual elements in \( T_2\)AlB\(_2\) with \( T = \text{Cr, Mn, Fe, Co, and Ni} \). The total density of states (DOS), scaled by 1/2, is also shown to compare. The total DOS of Fe\(_2\)AlB\(_2\) compares well with previously reported calculations [3]. Al-3s and B-2s states are located between \(-12 \text{ and } -7 \text{ eV} \) below the Fermi level \( E_F \). Al-3p states hybridize with \( T \) atoms at around \(-4 \text{ eV} \) below \( E_F \). For Mn\(_2\)AlB\(_2\), the Fermi level is located at a pseudogap in the AFM configuration, and the DOS at
The calculated hypothetical Co$_2$AlB$_2$ shows a weak magnetic moment of about 0.2 $\mu_B$/Co. The two peaks at $\pm0.1$ eV around the Fermi level, as shown in Fig. 4(d), will be pinched at $E_F$ in the non-spin-polarized calculation (not shown). Thus, the small spin polarization decreases the DOS at $E_F$ and stabilizes the system. The calculated Cr$_2$AlB$_2$ and hypothetical Ni$_2$AlB$_2$ are nonmagnetic and have small DOS at $E_F$. It is worth noting that Ni$_2$B$_{1-x}$ systems become magnetic only after $x > 0.75$.

Table III summarizes the lattice parameters, atomic positions, atomic moment of $T$ site, relative total energies, and critical temperatures of $T_2$AlB$_2$ with different magnetic configurations. The calculated lattice parameters and atomic positions agree well with experiments. The relaxed lattice parameters of $T_2$AlB$_2$ not only vary with element $T$ but also depend on the spin configuration. For Fe$_2$AlB$_2$, lattice parameters $a$ and $b$ decrease, and $c$ increases when the spin configuration changes from NM $\rightarrow$ AFM $\rightarrow$ FM. The calculated lattice parameters using the FM configuration agree the best with experiments. For Mn$_2$AlB$_2$, $b$ and $c$ increase when the spin configuration changes from NM $\rightarrow$ FM $\rightarrow$ AFM. Relaxed lattice parameters of $T_2$AlB$_2$ and hypothetical Ni$_2$AlB$_2$ have small DOS at $E_F$, and $T_2$AlB$_2$ is weakly ferromagnetic.

$E_F$ is smaller than in the FM configuration, which again suggests that the AFM configuration is more stable. The calculated magnetic moments of Fe, Al, and B sublattices, and (b) energy as functions of spin quantization axis rotation in Fe$_2$AlB$_2$. The inset in panel (b) shows the spin-resolved anisotropy of Fe-site spin-orbit coupling energy $K_{so}^{\sigma\sigma'} = \frac{1}{2}\langle V_{so}\rangle_{110} - \frac{1}{2}\langle V_{so}\rangle_{001}$.

FIG. 3. Variation of (a) atomic orbital magnetic moments of Fe, Al, and B sublattices, and (b) energy as functions of spin quantization axis rotation in Fe$_2$AlB$_2$. The inset in panel (b) shows the spin-resolved anisotropy of Fe-site spin-orbit coupling energy $K_{so}^{\sigma\sigma'} = \frac{1}{2}\langle V_{so}\rangle_{110} - \frac{1}{2}\langle V_{so}\rangle_{001}$.

FIG. 4. Atom- and spin-projected, scalar-relativistic partial densities of states (DOS) in (a) Cr$_2$AlB$_2$, (b) Mn$_2$AlB$_2$, (c) Fe$_2$AlB$_2$, (d) Co$_2$AlB$_2$, and (e) Ni$_2$AlB$_2$ calculated within GGA and using fully relaxed structures. The total DOS of the f.u. cell are scaled by $\frac{1}{2}$ to better compare. Cr$_2$AlB$_2$ and Ni$_2$AlB$_2$ are nonmagnetic. Mn$_2$AlB$_2$ is antiferromagnetic and Fe$_2$AlB$_2$ is ferromagnetic. Co$_2$AlB$_2$ is weakly ferromagnetic. Fermi energy $E_F$ is at 0 eV.
TABLE III. Lattice parameters, internal atomic positions, $y_{ij}$ and $y_{kl}$, on-site atomic magnetic moment of $T$ atoms, $m_T$ ($\mu_B$), relative total energy (meV/f.u.), and critical temperatures (Curie temperature in Fe$_2$AlB$_2$ or Néel temperature in Mn$_2$AlB$_2$), $T_C$ (K) in Fe$_2$AlB$_2$ with $T$ = Fe, Mn, Cr, Co, and Ni. $T$ atom occupies the 4j site (0 $y_{ij}$, 1/2) and B atom occupies the 4i (0 $y_{kl}$, 0) site.

| $T$     | $a$  | $b$  | $c$  | $y_{ij}$ | $y_{kl}$ | $m_T$ | $\Delta E$ | $T_C$ |
|---------|------|------|------|----------|----------|-------|-------------|-------|
| Cr      | 2.921| 11.034| 2.929| 0.3521   | 0.2057   | 0     |             | 0     |
| Expt.   | 2.937| 11.07 | 2.971| 0.352    | 0.220    |       |             |       |
| Expt.   | 2.937| 11.047| 2.968|          |          |       |             |       |
| Mn-NM   | 2.890| 11.050| 2.817| 0.3562   | 0.2060   | 0     |             | 0     |
| Mn-FM   | 2.892| 11.056| 2.826| 0.3551   | 0.2060   | 0.42  | -21.5       | 296   |
| Mn-AFM  | 2.887| 11.109| 2.830| 0.3547   | 0.2061   | 0.75  | -63.6       | 296   |
| Expt.   | 2.92 | 11.08 | 2.89  | 0.355    | 0.209    |       |             |       |
| Expt.   | 2.936| 11.12 | 2.912|          |          |       |             |       |
| Fe-NM   | 2.951| 11.261| 2.698| 0.3531   | 0.2065   | 0     |             | 0     |
| Fe-AFM  | 2.941| 11.212| 2.739| 0.3559   | 0.2070   | 1.06  | -97.9       |       |
| Fe-FM   | 2.915| 11.017| 2.851| 0.3537   | 0.2063   | 1.37  | -164.1      | 298   |
| Expt.   | 2.923| 11.034| 2.870| 0.3540   | 0.2071   |       |             |       |
| Co      | 2.962| 11.314| 2.689| 0.3541   | 0.2073   | 0.21  |             |       |
| Ni      | 2.979| 11.041| 2.843| 0.3586   | 0.2101   | 0     |             |       |

Relative to those of Fe$_2$AlB$_2$, the lattice parameter $a$ of $T_2$AlB$_2$ varies within 0.06 Å (2.2%) in the sequence of Mn < Fe < Cr < Co < Ni; $b$ varies within 0.30 Å (2.7%) in the sequence of Fe < Ni < Cr < Mn < Co; and parameter $c$ varies within 0.16 Å (5.7%) in the sequence of Co < Mn < Ni < Fe < Cr. Percentage-wise, the largest variation occurs with lattice parameter $c$. As we will show later, Fe$_2$AlB$_2$ has a much stronger magnetoelastic effect along the $c$ axis.

B. Alloys: $M$ and $T_C$ in Fe$_{2-x}$T$_x$AlB$_2$

To investigate how magnetic properties change with the 3d substitutions on Fe sites in Fe$_2$AlB$_2$, we first consider the chemical effect by neglecting the structure changes caused by substitution. The LMTO-ASA-CPA method is used to calculate the magnetization and the normalized effective exchange (or MFA estimation of $T_C$) in units of pure Fe$_2$AlB$_2$ in Fe$_{2-x}$T$_x$AlB$_2$ as functions of doping concentration $x$, with $T$ = Cr, Mn, Co, and Ni. The experimental lattice parameters and atomic positions of Fe$_2$AlB$_2$ are used and the results are shown in Fig. 3. All dopings decrease the magnetization and $T_C$ in Fe$_2$AlB$_2$. The component-resolved atomic spin moments $m_i$ in those alloys are shown in Fig. 6. For Mn doping, we also consider the AFM configuration and show the absolute values of component-resolved moments in Fig. 6(b).

Assuming the FM configuration, Mn has the slightest effect on the decrease of the magnetization and $T_C$. The Fe moment barely changes and even increases with a higher Mn content. The decrease of total magnetization is due to the dilution of Fe moments with smaller Mn moments. With a 25% Mn content, the calculated $T_C$ decreases by 20% while experiments found a larger $\Delta T_C = -30\%$. The assumption of FM configuration is logical when the Mn amount is small. However, at a higher Mn content, the AFM configuration should also be considered, given that pure Mn$_2$AlB$_2$ is more stable with...
the AFM configuration. Here we calculate the AFM configuration in CPA, by assuming the spin moments of 3$d$ atoms (both Fe and Mn components) are parallel within the ab plane and antiparallel between neighboring planes. As shown in Fig. 6(b), in comparison with the FM configuration, the AFM configuration gives larger Mn moments in the whole doping range and larger Fe moments at $x \geq 0.3$. Within CPA and without considering any lattice relaxation, the AFM configuration becomes more stable than the FM configuration with $x > 0.2$. Thus, the larger decrease of $T_C$ observed in experiments is likely caused by the forming of AFM phases in the samples. By systematically investigating solid solutions (Fe$_{1-x}$Mn$_x$)$_2$AlB$_2$, Chai et al. observed both NM and FM Mössbauer spectral components in all Mn-containing samples and attributed them to the clustering of Mn-rich and Fe-rich regions in the samples. Moreover, a spin-glass state has been observed at low temperature in (Fe$_{1-x}$Mn$_x$)$_2$AlB$_2$ with $x = 0.25$ and this phenomenon had been interpreted as the result of geometric frustration caused by the triangular configuration of magnetic atoms [5]. Here, we argue that it could be caused by the competition between the FM and AFM configurations along the c axis.

Given that a large DOS lies right above the Fermi level in the minority spin channel as shown in Fig. 4(c), it is not surprising that the electron doping, such as Co or Ni doping, decreases the magnetic moment on Fe sites. With a small amount of Co doping, the magnetization and $T_C$ decrease nearly linearly with Co content. Similar linear dependence of $T_C$ on Co content had been observed in experiments. As shown in Fig. 5(b), calculated ∆$T_C$ values agree very well with experiments [10]. With $0.4 < x < 0.9$, Co atoms in (Fe$_{1-x}$Co$_x$)$_2$AlB$_2$ have a small moment of $\sim 0.2 \mu_B$/Co, similar to the Co moment calculated in the fully relaxed structure of Co$_2$AlB$_2$ using FP. However, this small moment becomes unstable in ASA at $x = 1$.

In comparison to Co doping, Ni doping has a similar effect on decreasing $T_C$ and an even stronger effect on suppressing the magnetization in Fe$_2$AlB$_2$. As shown in Fig. 6(d), the atomic Ni moment in (Fe$_{1-x}$Ni$_x$)$_2$AlB$_2$ is small and coupled antiparallel with the Fe sublattice at small $x$, and negligible for $x > 0.3$.

In (Fe$_{1-x}$Cr$_x$)$_2$AlB$_2$, the Cr moment is small and parallel to the Fe sublattice. The maximum Cr moment of $0.2 \mu_B$/Cr occurs at $x = 0.5$. Like Mn, Cr doping has a smaller effect on decreasing the $T_C$ than Co and Ni. However, Cr doping is not likely to promote the FM $\rightarrow$ AFM transition, which may compromise the MCE as in the case of Mn doping [5]. Thus, it is worthwhile to investigate Cr doping, which may provide a useful approach to tune the $T_C$ and MCE in Fe$_2$AlB$_2$.

C. Effect of lattice distortion

Besides the chemical effect, the volume change caused by substitution may also affect the magnetic properties.

FIG. 7. Magnetization as functions of lattice parameters. Each of the three lattice parameters is varied with the other two being preserved. For the lattice distortion along the c axis, LDA results are also shown to compare. Magnetizations calculated in fully relaxed Fe$_2$(Al$_{0.5}$Mg$_{0.5}$)$_2$B$_2$, Fe$_2$(Al$_{0.5}$Si$_{0.5}$)$_2$B$_2$, and Fe$_2$(Al$_{0.5}$Ga$_{0.5}$)$_2$B$_2$ are also shown.

As shown in Table III the lattice parameters in $T_2$AlB$_2$ vary with the element $T$ and spin configuration. To have a rough idea on the magnetoelastic effect in Fe$_2$AlB$_2$, we calculate the magnetization dependence on the three lattice parameters, respectively. Starting from the fully relaxed structure, each of the three parameters is varied while the other two are kept constant. Interestingly, as shown in Fig. 7, the magnetoelastic effect in Fe$_2$AlB$_2$ is very anisotropic. The magnetization has a much stronger dependence on the lattice parameter $c$ than on $a$ or $b$. With $\Delta c = -6\%$, magnetization decreases by 35% within GGA and 60% within LDA.

This anisotropic magnetoelastic effect can be understood by investigating the electronic structure features near $E_F$ and their changes caused by the lattice distortion. The band structures of Fe$_2$AlB$_2$ in the majority and minority channels are shown in Fig. 8(a, c), respectively. The PDOS projected on Fe-3$d$ states and in two spin channels are shown in Fig. 8(b). Particularly of note is a narrow band right above $E_F$ in the minority spin channel. This band is found to consist almost entirely of a few d$_{xy}$ and d$_{x^2-y^2}$ ($m = \pm 2$) orbitals. The variations of PDOS with lattice parameter $c$ are shown in Fig. 9. The decreasing of parameter $c$ increases the bandwidth of the d$_{3z^2-1}$ state, which has a relatively large density right below $E_F$ in the majority spin channel. These antibonding d$_{3z^2-1}$ states, located between $-1.3$ eV and $E_F$, shift upward toward $E_F$ and become less occupied. Correspondingly, the aforementioned peak of $m = \pm 2$ states, located right above $E_F$ in the minority spin channel, become more occupied. As a result, the magnetization decreases. The Fe-d$_{yz}$ and d$_{xz}$ states ($m = \pm 1$) have small
FIG. 8. Band structure of Fe$_2$AlB$_2$ in (a) majority and (c) minority spin channels. Bands are with color weights, with blue identifying the Fe-$d_{3z^2-1}$ states, red the Fe-($d_{xy}, d_{x^2-y^2}$) states, and green everything else. PDOS [states (eV spin atom)$^{-1}$] projected on Fe-3$d$ states in two spin channels are shown in panel (b). The left and right portions of panel (b) show PDOS in the majority and minority spin channels, respectively. The horizontal dashed lines in all three panels indicate the Fermi level.

DOS around $E_F$ and contribute less to this magnetization change. With the further decrease of $c$ and then magnetization, the spin splitting becomes smaller, which quickly accelerates the decrease of magnetization as $\Delta c$ approaches to $-6\%$.

D. Dopings on B and Al sites

We also consider the substitutions of B and Al atoms with their neighboring elements in the periodic table: Be and C atoms on the B site, and Mg, Si, and Ga atoms on the Al site. The stabilities of those dopings are not well understood, and a careful and complete future investigation is desired. Here we focus on the possible effects of those dopings on the magnetization. Using various configurations of a ten-atom Fe$_2$AlB$_2$ unit cell, we substitute one B or Al atom with a dopant atom and fully relax the structures for Fe$_2$Al(B$_{0.75}$C$_{0.25}$)$_2$ with $Z$ = Be and C, and Fe$_2$(Al$_{0.5}$Z$_{0.5}$)B$_2$ with $Z$ = Mg, Si, and Ga. Their magnetizations calculated with the corresponding lowest energy configuration are denoted in Fig. 7 with respect to the change of lattice parameter $c$.

Only C doping on the B sites noticeably increases the lattice parameter $c$ and magnetization, while most other substitutions decrease the magnetization in Fe$_2$AlB$_2$. Both chemical effect and the magnetoelastic effect contribute to the magnetization enhancement. The lattice parameter $c$ increases by 1.6$\%$ and magnetization increases to $1.4\mu_B$/Fe in Fe$_2$Al(B$_{0.75}$C$_{0.25}$)$_2$. Unlike B, C has a small moment parallel to the Fe sublattice. Moreover, C doping increases the moments of neighboring Fe atoms by about $0.1\mu_B$/Fe.

For Si doping, without considering lattice relaxation, magnetization decreases by 6$\%$ in Fe$_2$(Si$_{0.5}$Al$_{0.5}$)B. The
relaxation decreases the lattice $c$ by 1.7%, and further decreases the magnetization by another 6%. Thus, both chemical effect and the magnetoelastic effect contribute to the decreasing of the magnetization. Be and Mg dopings have stronger effects on decreasing the magnetization. With Be and Mg dopings, the DOS peak right below $E_F$ in the majority spin shifts toward $E_F$ and becomes less occupied and the magnetization decreases to about 1.1 $\mu_B$/Fe. Ga doping has very small effect on the lattice parameters and the magnetization of Fe$_2$AlB$_2$.

IV. CONCLUSION

Using density functional theory, we investigated the intrinsic magnetic properties in T$_2$AlB$_2$ and their alloys. For Fe$_2$AlB$_2$, the $a$ axis is the easiest axis, while the $c$ axis is the hardest axis. For Mn$_2$AlB$_2$, we predict that the magnetic ground state is an AFM configuration, with the neighboring Mn layers being antiferromagnetically coupled along the $c$ axis. Co$_2$AlB$_2$ is weakly ferromagnetic, while Cr$_2$AlB$_2$ and Ni$_2$AlB$_2$ are nonmagnetic. All $3d$ substitutions decrease the magnetization and Curie temperature of Fe$_2$AlB$_2$ in the sequence of Mn $<$ Cr $<$ Co $<$ Ni. However, Mn promotes antiferromagnetism when its doping content is larger than 20%. The competition between the two configurations at critical compositions may be responsible for the spin-glass states observed in experiments. Unlike Mn, Cr doping is not likely to promote the AFM configuration, and may be useful in tuning $T_C$ in Fe$_2$AlB$_2$. The effects of strain and alloying on magnetic properties are also studied. A very strong anisotropic magnetoelastic effect is found. Magnetization in Fe$_2$AlB$_2$ becomes fragile and quickly decreases with the lattice parameter $c$, while it barely changes with $a$ and $b$. This effect is explained by the displacement of antibonding $d_{3z^2-1}$ states right below the Fermi level in the majority spin channel, and the filling of unoccupied $d_{xy}$ and $d_{x^2-y^2}$ states which have a sharp peak right above the Fermi level in the minority spin channel. Doping or applying pressure to modify the interlayer distance along the $c$ axis may provide an effective way to tune the magnetic properties in Fe$_2$AlB$_2$.

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