Competition between cubic and tetragonal phases in all-d-metal Heusler alloys, $X_{2-x}Mn_{1+x}V$ ($X =$ Pd, Ni, Pt, Ag, Au, Ir, Co; $x = 1, 0$): a new potential direction of the Heusler family

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Han, Yilin; Wu, Mengxin; Feng, Yu; Cheng, Zhenxiang; Lin, Tingting; Yang, Tie; Khenata, Rabah; and Wang, Xiaotian, "Competition between cubic and tetragonal phases in all-d-metal Heusler alloys, $X_{2-x}Mn_{1+x}V$ ($X =$ Pd, Ni, Pt, Ag, Au, Ir, Co; $x = 1, 0$): a new potential direction of the Heusler family" (2019). *Australian Institute for Innovative Materials - Papers*. 3609. [https://ro.uow.edu.au/aiimpapers/3609](https://ro.uow.edu.au/aiimpapers/3609)

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Competition between cubic and tetragonal phases in all-d-metal Heusler alloys, X2-xMn1+xV (X = Pd, Ni, Pt, Ag, Au, Ir, Co; x = 1, 0): a new potential direction of the Heusler family

Abstract
In this work, a series of all-d-metal Heusler alloys, X2 - x Mn 1 + x V (X = Pd, Ni, Pt, Ag, Au, Ir, Co; x; = 1, 0), were predicted by first principles. The series can be roughly divided into two categories: XMn 2 V (Mn-rich type) and X 2 MnV (Mn-poor type). Using optimized structural analysis, it is shown that the ground state of these all-d-metal Heusler alloys does not fully meet the site-preference rule for classic full-Heusler alloys. All the Mn-rich type alloys tend to form the L2 1 structure, where the two Mn atoms prefer to occupy the A (0, 0, 0) and C (0.5, 0.5, 0.5) Wyckoff sites, whereas for the Mn-poor-type alloys, some are stable with XA structures and some are not. The c/a ratio was also changed while maintaining the volume the same as in the cubic state to investigate the possible tetragonal transformation of these alloys. The Mn-rich Heusler alloys have strong cubic resistance; however, all the Mn-poor alloys prefer to have a tetragonal state instead of a cubic phase through tetragonal transformations. The origin of the tetragonal state and the competition between the cubic and tetragonal phases in Mn-poor alloys are discussed in detail. Results show that broader and shallower density-of-states structures at or in the vicinity of the Fermi level lower the total energy and stabilize the tetragonal phases of X2 MnV (X = Pd, Ni, Pt, Ag, Au, Ir, Co). Furthermore, the lack of virtual frequency in the phonon spectra confirms the stability of the tetragonal states of these Mn-poor all-d-metal Heusler alloys. This work provides relevant experimental guidance in the search for possible martensitic Heusler alloys in all-d-metal materials with less Mn and new spintronic and magnetic intelligent materials among all-d-metal Heusler alloys.

Keywords
cubic, tetragonal, phasesin, all-d-metal, heusler, between, pt, competition, ag, au, ir, 1, 0);, family, potential, x=, co;, direction, ni, alloys, pd, (x=, x2-xmn1+xv

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details
Han, Y., Wu, M., Feng, Y., Cheng, Z., Lin, T., Yang, T., Khenata, R. & Wang, X. (2019). Competition between cubic and tetragonal phases in all-d-metal Heusler alloys, X2-xMn1+xV (X = Pd, Ni, Pt, Ag, Au, Ir, Co; x = 1, 0): a new potential direction of the Heusler family. IUCrJ, 6 465-472.

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This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/3609
Competition between cubic and tetragonal phases in all-d-metal Heusler alloys, $X_{2-x}Mn_1+xV (X = \text{Pd, Ni, Pt, Ag, Au, Ir, Co}; x = 1, 0)$: a new potential direction of the Heusler family

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In this work, a series of all-d-metal Heusler alloys, $X_{2-x}Mn_1+xV (X = \text{Pd, Ni, Pt, Ag, Au, Ir, Co}; x = 1, 0)$, were predicted by first principles. The series can be roughly divided into two categories: $XMn_2V$ (Mn-rich type) and $X_2MnV$ (Mn-poor type). Using optimized structural analysis, it is shown that the ground state of these all-d-metal Heusler alloys does not fully meet the site-preference rule for classic full-Heusler alloys. All the Mn-rich type alloys tend to form the L2$_1$ structure, where the two Mn atoms prefer to occupy the A (0, 0, 0) and C (0.5, 0.5, 0.5) Wyckoff sites, whereas for the Mn-poor-type alloys, some are stable with $XA$ structures and some are not. The $c/a$ ratio was also changed while maintaining the volume the same as in the cubic state to investigate the possible tetragonal transformation of these alloys. The Mn-rich Heusler alloys have strong cubic resistance; however, all the Mn-poor alloys prefer to have a tetragonal state instead of a cubic phase through tetragonal transformations. The origin of the tetragonal state and the competition between the cubic and tetragonal phases in Mn-poor alloys are discussed in detail. Results show that broader and shallower density-of-states structures at or in the vicinity of the Fermi level lower the total energy and stabilize the tetragonal phases of $X_2MnV (X = \text{Pd, Ni, Pt, Ag, Au, Ir, Co})$. Furthermore, the lack of virtual frequency in the phonon spectra confirms the stability of the tetragonal states of these Mn-poor all-d-metal Heusler alloys. This work provides relevant experimental guidance in the search for possible martensitic Heusler alloys in all-d-metal materials with less Mn and new spintronic and magnetic intelligent materials among all-d-metal Heusler alloys.

1. Introduction

Heusler alloys have been a research hotspot for more than 100 years, gaining the attention of researchers due to their excellent properties and wide range of applications. High Curie temperatures ($T_C$), tunable electronic structure, suitable lattice constants for semiconductors and various magnetic properties (Manna et al., 2018) make Heusler alloys ideal materials for spin-gapless semiconductors (Wang et al., 2018; Bainsla et al., 2015; Gao et al., 2019), half-metallic materials (Shigeta et al., 2018; Han et al., 2019; Khandy et al., 2018) and shape memory alloys (Yu et al., 2015; Odaira et al., 2018; Li et al., 2018a,b; Carpenter & Howard, 2018). Normally, there are three types of Heusler alloys: half-Heusler-type $XYZ$ (Makongo et al., 2011; Anand et al., 2018; Zhang et al., 2016; Hou et al., 2015), full-Heusler-type $X_2YZ$ (Akriche et al., 2017;
Babiker et al., 2017; Li et al., 2018a,b) and the equiatomic quaternary Heusler XYMZ materials (Bahramian & Ahmadian, 2017; Qin et al., 2017; Wang et al., 2017; Feng et al., 2018) with stoichiometry 1:1:1:1, where the X, Y and M atoms are usually transition-metal atoms, whereas the Z atom is a main-group element. However, some new Heusler alloys have emerged, adding novel theoretical and experimental findings to Heusler’s research. As DO$_2$-type X$_2$Z (Liu et al., 2018) and C1$_{5}$-type X$_2$Z (Wang et al., 2016) alloys are converted from full-Heusler X$_2$YZ and half-Heusler XYZ alloys, all-d-metal Heusler alloys (Wei et al., 2015, 2016; Han et al., 2018; Ni et al., 2019), whose atoms are entirely transition-metal elements, have created new potential for Heusler alloys. Although some all-d-metal Heusler alloys like Mn$_2$AuAg and Zn$_2$CuAu (Muldawer, 1966; Murakami et al., 1980) have been studied earlier, their nonmagnetic structures limited their applications in many magnetic fields for shape memory effects. Recently, Wei et al. (2015) synthesized a new all-d-metal Heusler system Ni$_{50}$Mn$_{50}$Ti$_{1}$, and what is more, a possible martensitic transformation could be observed in Co-doped Ni–Mn–Ti phases. Wei et al. (2016) also synthesized Mn$_{50}$Ni$_{50-2x}$Co$_{x}$Ti$_{10}$ (x = 8 or 9.5) all-d-metal Heusler systems and magnetoostructural martensitic transformations can be observed near room temperature. Based on this experimental work (Wei et al., 2016), a very detailed theoretical study on understanding the magnetic structural transition in the all-d-metal Heusler alloy Mn$_2$Ni$_{1+2x}$Co$_{2x}$Ti$_{0.5}$ has been carried out by Ni and coworkers (Ni et al., 2019). We must note, however, that research on this aspect is very rare. Recently, some interesting work brought to our attention by Tan research on this aspect is very rare. Recently, some interesting work brought to our attention by Tan et al. (2019) reported that all-d-metal alloys may not satisfy the site preference rule as do most classic full-Heusler alloys. Therefore, searching for new magnetic all-d-metal Heusler alloys and investigating their site occupation is necessary.

Examining recent studies of Heusler alloys, researchers emphasized the cubic state over the tetragonal phase, which limits progress in finding better tetragonal Heusler alloys. However, tetragonal phases are more likely to demonstrate large perpendicular magnetic anisotropy than the cubic state – the key to spin-transfer torque devices (Balke et al., 2007). Additionally, tetragonal states have large magneto-crystalline anisotropy (Salazar et al., 2018; Matsushita et al., 2017), large intrinsic exchange-bias behaviour (Felser et al., 2013; Nayak et al., 2012) and a high Curie temperature. To better apply Heusler alloys to actual fields, it is also important to study their tetragonal state and the competition between cubic and tetragonal states.

Based on the above information, in this work we focused on a series of all-d-metal Heusler alloys, X$_{2-x}$Mn$_{1+x}$V (X = Pd, Ni, Pt, Ag, Au, Ir, Co; x = 1, 0). Our goals were to further strengthen the study of all-d-metal Heusler alloys and investigate their magnetic properties, electronic structures and site preference via first principles. We provide an in-depth discussion of their tetragonal transformations to find a stable tetragonal phase in the search for better applications in spintronics. We also explain and prove the stability of the tetragonal phases with the help of density of states (DOS) and phonon spectra.

2. Computational methods

Under the framework of density functional theory (Becke, 1993), with the help of CASTEP code, we conducted first-principle band computations using the plane-wave pseudo-potential method (Troullier & Martins, 1991). To describe the interaction between electron-exchange-related energy and the nucleus and valence electrons, the Perdew–Burke–Ernzerhof function of the generalized gradient approximation (Perdew et al., 1996; Hernández-Haro et al., 2019) and ultra-soft (Al-Douri et al., 2008) pseudo-potential were used, respectively. We employed a 450 eV cut-off energy, a Monkhorst–Pack 12 × 12 × 12 grid for the cubic structure and a 12 × 12 × 15 grid for the tetragonal structure of the first Brillouin region. The self-consistent field tolerance was 10$^{-6}$ eV. The phonon energy calculation of Mn-poor type X$_2$MnV (X = Pd, Ni, Pt, Ag, Au, Ir, Co) was performed in Nano Academic Device Calculator (Nanodcal) code (Taylor et al., 2001).

3. Results and discussion

3.1. Site preference and magnetism of cubic all-d-metal Heusler alloys, X$_{2-x}$Mn$_{1+x}$V (X = Pd, Ni, Pt, Ag, Au, Ir, Co; x = 1, 0)

The site-preference rule (Luo et al., 2016; Ma et al., 2017; Wei et al., 2017) for classic full-Heusler X$_2$YZ alloys provides...
Heusler alloys of essential to study the site occupation of these all-depend strongly on a highly ordered structure. Hence, it is rily conform to the site-preference rule. The desired properties elements without main-group atoms, so they do not necessa-

Heusler alloys are composed entirely of transition-metal elements and main-group elements; however, the situation is not the same as in all-

Table 1

| Compound X_2YZ | ΔE (eV per cell) | Structure | a (Å) | Mt (μμ_B per formula unit) | MY (μμ_B) | MV (μμ_B) | MX-1 (μμ_B) | MX-2 (μμ_B) | Stable structure |
|----------------|------------------|-----------|-------|-----------------------------|-----------|-----------|-------------|-------------|-----------------|
| Pd_2MnV       | 0.29             | Inverse   | 6.18  | 1.37901                     | 3.12      | -1.89     | -0.04       | 0.2         | XA              |
| Mn_2PdV       | -0.61            | Regular   | 6.11  | 4.52573                     | 3.71      | 0.26      | 0.28        | 0.28        | L2_1            |
| Ni_2MnV       | 0.25             | Inverse   | 5.75  | 1.76204                     | 2.09      | -0.09     | 0.04        | 0.52        | XA              |
| Mn_2NiV       | -0.40            | Inverse   | 5.75  | 4.68429                     | 0.35      | 0.77      | -0.84       | 2.64        | L2_1            |
| Ag_2MnV       | 0.05             | Inverse   | 6.22  | 0.51632                     | 2.96      | -2.29     | -0.17       | 0.01        | XA              |
| Mn_2AgV       | -0.64            | Inverse   | 6.25  | 4.05781                     | 3.75      | -2.54     | -0.07       | -0.07       | L2_1            |
| Au_2MnV       | 0.16             | Inverse   | 6.22  | 4.34356                     | 0.12      | -1.98     | 3.10        | 3.10        | XA              |
| Mn_2AuV       | -0.92            | Inverse   | 6.28  | 0.97787                     | 3.15      | -2.11     | -0.13       | 0.07        | XA              |
| Co_2MnV       | -0.20            | Inverse   | 6.33  | 4.86251                     | 3.70      | 0.97      | 0.15        | 0.15        | XA              |
| Mn_2CoV       | -0.16            | Inverse   | 6.33  | 3.97767                     | 3.15      | -2.11     | -0.13       | 0.07        | XA              |
| Pt_2MnV       | -0.18            | Inverse   | 6.25  | 4.68044                     | 0.21      | -1.89     | 3.27        | 3.27        | XA              |
| Mn_2PtV       | -0.53            | Inverse   | 6.56  | 3.85062                     | 1.83      | -0.6      | 1.06        | 1.57        | L2_1            |
| Ir_2MnV       | -1.05            | Inverse   | 6.45  | 4.11403                     | 3.01      | -1.4      | 0.99        | 1.11        | L2_1            |
| Mn_2IrV       | -0.22            | Inverse   | 5.96  | 3.78006                     | 0.52      | 0.62      | -0.39       | 3.03        | L2_1            |

fundamental guidance for their theoretical design and study of properties. When the X atoms carry the most valence electrons, X tends to occupy the A (0, 0, 0) and C (0.5, 0.5, 0.5) Wyckoff sites, and Y atoms, having relatively less valence electrons, prefer the B site (0.25, 0.25, 0.25). The Z atoms, having the least valence electrons, tend to be located at the D site (0.75, 0.75, 0.75), forming the L2_1 type structure [or Cu_2MnAl type, with space group Fm3m (No. 225)] as shown in Fig. 1(c). Another situation occurs when Y has the most valence electrons; the XA type [or the Hg_2CuTi/inverse type, with space group F43m (No. 216)] is usually formed [see Fig. 1(a)]. The full-Heusler alloys consist of both transition-metal elements and main-group elements; however, the situation is not the same as in all-d-metal Heusler alloys. All-d-metal Heusler alloys are composed entirely of transition-metal elements without main-group atoms, so they do not necessarily conform to the site-preference rule. The desired properties depend strongly on a highly ordered structure. Hence, it is essential to study the site occupation of these all-d-metal Heusler alloys of X_2-xMn_1+xV (X = Pd, Ni, Pt, Ag, Au, Ir, Co; x = 1, 0).

Given the above two site occupations, we computed ΔE = E(L2_1) − E(XA) (eV per cell) of all these X_2-xMn_1+xV Heusler alloys and the results are shown in Fig. 2. If ΔE > 0, the total energy of the L2_1-type is more than that of XA, indicating that the XA state is more stable than the L2_1 state. Another situation is the L2_1 type. Fig. 2 shows that there are four alloys exhibiting XA-stable states: Ni_2MnV, Au_2MnV, Pd_2MnV and Ag_2MnV, whereas the rest of X_2-xMn_1+xV are L2_1-type. However, when the total energy difference between XA and L2_1 phases is quite small, the two states may co-exist. So, Ag_2MnV is hard to separate into two states, whereas Mn_2AuV and Ir_2MnV can be separated more easily into the L2_1 state due to the largest |ΔE| (>0.8 eV), as also outlined in Table 1.

Now we discuss the application of the site-preference rule in X_2-xMn_1+xV all-d-metal Heusler alloys. For all X_2-xMn_1+xV alloys, X carries more valence electrons than Mn and V, so the Mn-poor type should form the L2_1 state. X atoms tend toward the A and C sites, and Mn prefers the B sites. The Mn-rich alloys should be XA-type: two Mn atoms occupy the A and B sites; and the remaining X atoms occupy the C sites. When the total valence electrons of Mn and V are almost the same, X could prefer to be located at the A and C sites, forming the L2_1 state. Therefore, a highly ordered structure is essential for the desired properties of Heusler alloys.
sites according to the site-preference rule. However, in our calculations, the Mn-rich alloys fully disobey the site-preference rule, and some Mn-poor types meet the rule whereas others do not, suggesting that the site-preference rule does not apply to all of the all-d-metal Heusler alloys.

Finally, we come to study the magnetic properties of these alloys in the cubic phase; the total magnetic moments of these all-d-metal Heusler alloys are shown in Table 1. Mn provides the mainly magnetic moments both in XA-type and L2₁-type, and the magnetic moments of two Mn atoms in Mn-rich alloys are always identical due to the fact that the surrounding environments of the two Mn atoms are the same in the L2₁ phases.

3.2. Tetragonal transformations in all-d-metal Heusler alloys, $X_2$MnV ($X = $ Pd, Ni, Pt, Ag, Au, Ir, Co)

In Fig. 3, the competition between the cubic and tetragonal phases in all-d-metal Heusler alloys $X_{2-x}$Mn$_{1+x}$V ($X = $ Pd, Ni, Pt, Ag, Au, Ir, Co; $x = 1, 0$) was exhibited. We maintained the volume at the same value as in the cubic ground state and simultaneously regulated the $c/a$ ratio to search for a stable tetragonal state. Two types of tetragonal structures, i.e. inverse tetragonal Heusler $X_2$YV and regular tetragonal Heusler $X_2$YV can be found in Figs. 1(b) and 1(d). For certain $X$ elements, Mn-rich and Mn-poor types exhibit different cubic resistances to tetragonal distortion. All the Mn-poor $X_2$MnV ($X = $ Pd, Ni, Pt, Ag, Au, Ir, Co) all-d-metal Heusler alloys have possible tetragonal transformations, obtaining points with lower total energies, which may be a possible martensitic phase. Conversely, most of the Mn-rich alloys do not have tetragonal deformation or too small a degree of tetragonal distortion.

Figure 3

(a)–(g) Relationship between the total energy difference $\Delta E = E(c/a) - E(c/a = 1.0)$ and the $c/a$ ratio for $X_{2-x}$Mn$_{1+x}$V ($X = $ Pd, Ni, Pt, Ag, Au, Ir, Co; $x = 1, 0$).

Figure 4

$\Delta E = E_C - E_T$ per formula unit as a function of $X_{2-x}$Mn$_{1+x}$V.
To further study the tetragonal transformation of different \( X \) elements, we calculated the \( \Delta E = E_{\text{cubic}} - E_{\text{tetragonal}} \) (eV per cell) for all the Mn-poor \( X_2\text{MnV} \ (X = \text{Pd}, \text{Ni}, \text{Pt}, \text{Ag}, \text{Au}, \text{Ir}, \text{Co}) \) structures and two Mn-rich structures (\( \text{Mn}_2\text{AgV} \) and \( \text{Mn}_2\text{AuV} \)) with tetragonal deformation (see Fig. 4). However, we found that although the two Mn-rich alloys have relatively lower energy states compared with the cubic state, the degree of the tetragonal distortion is too small (\( \Delta E < 0.1 \text{ eV} \)) (Wu et al., 2019) to obtain a stable phase. The larger the value of \( \Delta E \), the easier tetragonal distortion occurs.

Notably, the value of \( \Delta E \) of \( \text{Au}_2\text{MnV} \) is 0.49 eV, more than four times the standard \( \text{Mn}_2\text{Ga} \) and \( \text{Mn}_2\text{FeGa} \) \( \Delta E \) (Liu et al., 2018) at 0.12 eV and 0.14 eV per formula unit, respectively.

Apart from the tetragonal deformation, uniform strain should also be considered. We chose \( \text{Ag}_2\text{MnV} \) and \( \text{Pd}_2\text{MnV} \) as examples to study the influence of volume change. In Fig. 5, we applied values of \(-3, -2, -1, 0, +1, +2\) and \(+3\% \text{ of } V_{\text{equilibrium}}(\text{Opt})\) for detailed discussion. For \( \text{Ag}_2\text{MnV} \), the absolute value of the total energy decreases, resulting in the decline of the absolute value of \( \Delta E = E_{\text{cubic}} - E_{\text{tetragonal}} \) (eV per cell) with a degree of around 0.32 to 0.18 eV per formula unit as volume expansion from \( V_{\text{opt}} - 3\% V_{\text{opt}} \) to \( V_{\text{opt}} + 3\% V_{\text{opt}} \), as shown in Fig. 5(c). Regardless of the volume changes, the possible tetragonal phases occur at \( c/a = 1.40 \). The situation is similar in \( \text{Pd}_2\text{MnV} \) [see Fig. 5(b)].

3.3. The origin of the tetragonal state of Mn-poor \( X_2\text{MnV} \ (X = \text{Pd}, \text{Ni}, \text{Pt}, \text{Ag}, \text{Au}, \text{Ir}, \text{Co}) \) alloys

All-d-metal Heusler alloys are entirely composed of transition-metal elements possessing \( d \) states. The peak-and-valley character of the DOS in these alloys occurs due to the highly localized \( d \) states and the van Hove singularities at the band

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**Figure 5**
Total energy as a function of the \( c/a \) ratio for (a) \( \text{Ag}_2\text{MnV} \) and (b) \( \text{Pd}_2\text{MnV} \) with contraction/expansion of the unit-cell volume. (c) \( \Delta E_{\text{Ag}} \) as functions of the \( V_{\text{opt}} + X\%V_{\text{opt}} \ (x = -3, -2, -1, 0, 1, 2, 3) \) for \( \text{Ag}_2\text{MnV} \) and \( \text{Pd}_2\text{MnV} \).

**Figure 6**
The DOS of cubic and tetragonal states for (a) \( \text{Ag}_2\text{MnV} \), (b) \( \text{Au}_2\text{MnV} \) and (c) \( \text{Pt}_2\text{MnV} \). (d) The total and atomic DOS in inverse cubic and tetragonal states for \( \text{Ag}_2\text{MnV} \).
edges of the d states (Faleev et al., 2017a). The peak-and-valley character in the cubic state is one of the prerequisite conditions for X₂MnV to have tetragonal distortion (the ‘smooth shift’ of DOS channels relative to E_F when adding valence electrons to the system). According to Faleev et al. (2017a), the Fermi level of the cubic system is usually located at the middle of the DOS peak. However, the high DOS near E_F causes high energy, which leads to poor structural stability in the cubic state (Faleev et al., 2017a,b; Wu et al., 2019).

To complete an in-depth analysis of the reason for the tetragonal transformation of all-d-metal Heusler alloys of X₂MnV (X = Pd, Ni, Pt, Ag, Au, Ir, Co), we selected some Mn-poor-type alloys, Ag₂MnV, Au₂MnV and Pt₂MnV, as examples. We first look at Fig. 6(a). In the spin-up channel of Ag₂MnV, a peak at the Fermi level changes into a valley through tetragonal deformation, with lower total energy by 0.56 states per eV. In the other channel, a high peak at around −0.5 eV is released, lowering the peak DOS at or in the vicinity of E_F, which explains the stability of the tetragonal state. Similar situations can be found in Au₂MnV [Fig. 6(b)] and Pt₂MnV [Fig. 6(c)]. Two DOS peaks at E_F in the spin-up shift to lower energy; thus, a low energy DOS valley is located in the Fermi level after the tetragonal distortion of Au₂MnV. Three peaks about E_F invert into a smooth valley in the spin-up channel of Pt₂MnV in conjunction with a high peak turning into a low peak in the spin-down. We examined this to help these alloys lower the total energy then stabilize these alloys via tetragonal transformation.

Why would a high DOS (around the Fermi level) in the cubic phase become lower during tetragonal transformation? The reasons can be summarized as follows (Faleev et al., 2017a). (i) Through tetragonal distortion, the symmetry in the

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Figure 7
(a)–(g) Phonon dispersion curves of tetragonal X₂MnV (X = Pd, Ni, Pt, Ag, Au, Ir, Co; x = 1, 0).
Brillouin zone is destroyed, which results in some \( k \)-points being inequivalent, causing a less peaky structure for the DOS structure. (ii) After tetragonal distortion, the symmetry of the system will be lower, and thus the degeneration of some high-symmetry \( k \)-points in the vicinity of Fermi level can be released. (iii) After tetragonal distortion, the bands, which are derived from the orbits that overlap in the direction of crystal contraction, become broader.

Then, we studied the total and atomic DOS of inverse cubic and tetragonal states, as shown in Fig. 6(d). Whether the cubic or the tetragonal structures exhibit metallic properties is explained by the definite value of the \( E_F \) in both the majority and minority of DOS. In the cubic state of \( \text{Ag}_2\text{MnV} \), the DOS in spin-up mainly comes from the atoms Mn and V, indicating that the total magnetic moment in the cubic phase of \( \text{Ag}_2\text{MnV} \) is mostly contributed by Mn and V atoms. In both spin channels, the Mn and V atoms both have strong spin splitting in different directions, resulting in a stable tetragonal phase. The DOS of the Mn and V atoms mainly forms the TDOS structure in spin-up and spin-down channels, and the opposite spin splitting of Mn and V atoms offset each other, resulting in a small total magnetic moment (~0.43 \( \mu_B \)). The calculated magnetic properties of tetragonal phases of these alloys have been listed in Table 2. One can see that for the regular tetragonal type, all \( X \) atoms have the same atomic magnetic moments due to the fact that they are in the same atomic environment, whereas for the inverse tetragonal type, the atomic magnetic moments of X-1 and X-2 are not the same.

Finally, we introduced phonon spectra to further demonstrate the stability of seven tetragonal-type Mn-poor all-\( d \)-metal Heusler alloys, \( X_2\text{MnV} \) (\( X = \text{Pd, Ni, Pt, Ag, Au, Ir, Co} \)). Unexpectedly, as shown in Fig. 7, there is no imaginary frequency in the phonon spectra of all seven alloys, verifying the stability of their tetragonal states.

### 4. Conclusions

In this study, we highlighted a new potential direction for Heusler alloys – all-\( d \)-metal Heusler alloys – by investigating \( X_2 - x\text{Mn}_1 + x \text{V} \) (\( X = \text{Pd, Ni, Pt, Ag, Au, Ir, Co; } x = 1, 0 \)). Firstly, we examined their atomic occupancy in the cubic phase, finding the well known site-preference rule does not apply to all of these all-\( d \)-metal Heusler alloys. Then, we studied changes in the \( c/a \) ratio and the effect of uniform strain for the tetragonal transformation of \( X_2 - x\text{Mn}_1 + x \text{V} \). Surprisingly, all the Mn-poor alloys undergo possible tetragonal distortion and attain a stable tetragonal phase, whereas Mn-rich alloys do not have, or have only to a small extent, tetragonal distortion. Additionally, with the help of the DOS, we conducted in-depth research and provided discussion on the reasons for the transformation of the cubic phase to the tetragonal phase. Finally, we demonstrated the stability of the tetragonal state of Mn-poor all-\( d \)-metal alloys via the phonon spectra.

### Funding information

This research was funded by Fundamental Research Funds for the Central Universities (grant No. XDJK2019D033), the Program for Basic Research and Frontier Exploration of Chongqing City (grant No. cstc2018cyjA0765) and the National Natural Science Foundation of China (grant No. 51801163).

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