

Article

Evolution of Magnetic and Electronic Properties Across the (Co, Rh, Ir)₂(V, Cr, Mn)(Ti, Zr, Hf) All-*d* Heusler Compounds

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Abstract

The emergence of all-*d*-metal Heusler alloys has opened up new pathways for the design of advanced functional materials. In this work, we employ first-principles electronic structure calculations to systematically investigate the electronic and magnetic properties of 27 all-*d*-metal Heusler compounds following the stoichiometry X_2YZ , where $X = \text{Co, Rh, Ir}$, $Y = \text{V, Cr, Mn}$, and $Z = \text{Ti, Zr, Hf}$. Electronic band structure calculations show a consistent minority-spin pseudogap across the series, the width and characteristics of which are strongly dependent on the *d*-band broadening introduced by 4*d* (Rh, Zr) and 5*d* (Ir, Hf) transition metals. Magnetically, these materials largely follow the $M_t = Z_t - 24$ Slater–Pauling rule, driven by exactly 12 occupied minority-spin bands at the Γ point. Notably, substituting Co with Rh or Ir significantly redistributes the magnetization, drastically reducing the *X*-site spin magnetic moment while amplifying the spin magnetic moments on the *Y*-site atoms. This study provides a comprehensive understanding of the interplay between structural symmetry, orbital hybridization, and magnetism in all-*d*-metal Heuslers, highlighting their promise for future spintronic applications.

Keywords: Heusler compounds; ab initio calculations; first principles; electronic structure; ferromagnetic materials; Slater–Pauling rule

1. Introduction

The origin of Heusler compounds dates back to the early 20th century when German metallurgist Fritz Heusler discovered that the Cu_2MnAl alloy exhibited remarkable magnetic properties despite containing no ferromagnetic elements [1,2]. Subsequent advancements in structural characterization revealed that these compounds crystallize in a face-centered cubic (f.c.c.) lattice, analogous to the structures found in prominent semiconductors such as silicon (Si) and gallium arsenide (GaAs). Collectively termed Heusler alloys [3,4], this family of intermetallics is renowned for high Curie temperatures and diverse electronic profiles. The standard full-Heusler compounds, exemplified by Co_2MnSi , typically follow the X_2YZ stoichiometry and crystallize in the $L2_1$ structure ($Fm\bar{3}m$) [3,4]. However, when the valence of the *X* element is lower than that of *Y*, the system may adopt the *XA* (or “inverse”) structure ($F\bar{4}3m$), leading to distinct physical phenomena.

A particularly significant subclass is the half-metallic magnets [5]. These materials act as metals for one spin channel while exhibiting a semiconducting gap for the other, resulting in 100% spin polarization at the Fermi level [6]. Their total spin magnetic moment (in μ_B) typically follows the Slater–Pauling rule, yielding integer values that facilitate predictable magnetic behavior [7]. Such properties make Heusler alloys premier candidates for spintronic and magnetoelectronic applications [8–12]. In recent years, the discovery



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of new functional Heusler materials has been accelerated by ab initio (first-principles) calculations and high-throughput databases [13–20]. Furthermore, machine learning models trained on vast crystallographic datasets have successfully predicted the synthesizability of both regular and inverse alloys, as demonstrated by the recent realization of $Ru-Ga-X$ ($X = Ti - Co$) systems [21].

Traditional full-Heusler alloys generally incorporate a metalloid at the Z site. However, a modern paradigm shift has emerged through the development of all- d -metal Heusler alloys, where the metalloid is replaced by a transition metal [22–37]. These systems are particularly noteworthy for their susceptibility to martensitic transformations, which are critical for magnetic shape memory and caloric applications. Recent high-throughput screenings have expanded this field significantly, identifying 686 (meta-)stable compounds and elucidating the relationship between intermetallic bonding, structural stability, and mechanical properties [32]. This research has also investigated anomalous Hall and Nernst conductivities, providing a roadmap for optimizing transport properties. Subsequent studies have further expanded these databases, specifically targeting the magnetocaloric potential of all- d Heusler frameworks [38,39].

In our previous research, we systematically investigated the electronic and magnetic properties of all- d -metal Heusler compounds through a series of first-principles studies [40–42]. In our initial work, we explored the Fe_2CrZ and Co_2CrZ ($Z = Sc, Ti, V$) systems, identifying high spin polarization and a significant pseudogap at the Fermi level [40]. While these all- d -metal Heusler compounds exhibit a Slater–Pauling-like behavior [7], the 12 minority-spin bands cross the Fermi level away from the Γ point, preventing the formation of a true half-metallic gap [40] and resulting in a region of very low minority-spin density of states around the Fermi level, usually referred to as a pseudogap. The pseudogap should not be confused with the so-called “nearly” half-metallic materials where a real energy gap exists but the Fermi level slightly crosses the valence or conduction minority-spin electronic band structure. We then extended our investigation to Co_2YZ compounds where the valence follows the $Co > Y > Z$ sequence, discovering that these materials exhibit remarkably high spin magnetic moments—reaching $9 \mu_B$ for Co_2FeMn —and generally follow the Slater–Pauling rule due to the presence of a deep pseudogap [41]. Most recently, we expanded this scope to include $4d$ and $5d$ transition metals, studying $(Co, Rh, Ru)_2MnZ$ compounds [42]. This work revealed that while Co- and Ru-based systems largely adhere to Slater–Pauling behavior, Rh-based compounds exhibit significant deviations, especially when paired with heavier Z elements.

Building upon these previous studies, the present work is designed not merely as a systematic compositional extension, but as a controlled investigation of how the progressive replacement of $3d$ elements by $4d$ and, in particular, $5d$ transition metals modifies the electronic and magnetic mechanisms of all- d -metal full-Heusler compounds. In contrast to our earlier works, which focused either on all- $3d$ systems or on more restricted combinations involving selected $4d/5d$ elements, the present 27-compound set, $(Co, Rh, Ir)_2(V, Cr, Mn)(Ti, Zr, Hf)$, allows us to separate the effects of the X-site substitution $Co \rightarrow Rh \rightarrow Ir$, the Y-site valence variation $V \rightarrow Cr \rightarrow Mn$, and the Z-site replacement $Ti \rightarrow Zr \rightarrow Hf$ within the same structural prototype. The central question addressed here is whether the spatially more extended $5d$ orbitals introduce qualitatively new electronic or magnetic phenomena, or whether they mainly renormalize the trends already observed in $3d$ - and $4d$ -based all- d -metal Heuslers. Our results show that the $5d$ elements do not generate a new symmetry-driven minority-spin gap or a different Slater–Pauling mechanism. Instead, they enhance d -band broadening and orbital hybridization, smooth and narrow the minority-spin pseudogap, and strongly redistribute the spin magnetic moment from the X sublattice toward the V, Cr, or Mn atoms. Thus, the novelty of the present work lies in identifying

5d-orbital delocalization as a key tuning parameter controlling the robustness of the pseudogap and the sublattice-resolved magnetization in all-d-metal Heusler alloys. Through first-principles calculations, we therefore assess not only the adherence of these compounds to the $M_t = Z_t - 24$ Slater–Pauling rule, but also the microscopic origin of deviations from ideal integer moments and the extent to which 4d and 5d chemistry can be used to tailor spin polarization in Heusler-based spintronic and magnetoelectronic materials.

2. Computational Method and Calculation Details

Our investigation into the ground-state properties of all-d-metal Heusler compounds is based on first-principles electronic structure calculations. We employed the full-potential non-orthogonal local-orbital minimum-basis (FPLO) method [43,44], utilizing the generalized gradient approximation (GGA) for the exchange-correlation functional as parameterized by Perdew, Burke, and Ernzerhof (PBE) [45]. Scalar-relativistic formalism was employed to account for the relativistic corrections. To ensure the accuracy of our calculations, the charge density in the primitive unit cell and the total energy are converged to the 8th and 10th decimal points, respectively. Furthermore, a dense grid of **k**-points, specifically a $20 \times 20 \times 20$ grid, conforming to the Monkhorst–Pack scheme [46], is utilized for the integrals in reciprocal space. In our calculations, we have not included the spin–orbit coupling. This should not influence our results since the studied compounds contain transition metal atoms and the lattice is actually a cubic compound of very high symmetry, as discussed below, resulting in vanishing magnetocrystalline anisotropy energy. Moreover, we expect that electronic correlations should also not be important and can be safely neglected. The compounds under study have 27, 28 or 29 valence electrons per unit cell, and previous calculations on full-Heusler compounds have revealed that only compounds with 30 or more valence electron correlation effects become sizeable [47].

Full-Heusler compounds typically crystallize in either the regular $L2_1$ ($Fm\bar{3}m$) or the inverse XA ($F\bar{4}3m$) structure, distinguished by the atomic site occupancy sequence within the unit cell. In the regular $L2_1$ lattice, the two *X* atoms (e.g., Co, Rh, or Ir) occupy equivalent sublattices and possess identical nearest and next-nearest neighbor environments. Conversely, in the *XA* structure, these *X* atoms occupy non-equivalent sites, resulting in a reduction in symmetry. Previous systematic studies [41,42] have demonstrated that for the specific all-d compounds addressed here, the $L2_1$ structure is energetically more favorable than the *XA* phase. The $L2_1$ arrangement is illustrated in Figure 1, using Rh_2CrZr as a prototype. In this configuration, the two Rh atoms are equivalent; although their next-nearest neighbor environments are rotated by 90° relative to one another, they both occupy sites with octahedral symmetry. The overall symmetry of the crystal remains tetrahedral, a factor that significantly influences the electronic band structures discussed in the following section.

The equilibrium lattice constants for all studied compounds were retrieved from the Open Quantum Materials Database (OQMD) [48–50]. The reliability of the OQMD data for these systems is well-established; for instance, the OQMD lattice constants for Co_2CrZ ($Z = \text{Sc}, \text{Ti}, \text{V}$) differ by less than 1% from the values obtained via explicit total-energy minimization in Reference [40]. Table 1 summarizes the OQMD-derived lattice constants, formation energies (E_{form}), and distances from the convex hull (E_{hull}).

Thermodynamic stability is primarily assessed through E_{form} , which must be negative for a compound to be energetically favorable relative to its constituent elements in their bulk phases. With the exception of Co_2CrZr , all compounds investigated here exhibit negative formation energies in the $L2_1$ structure. However, a negative E_{form} is a necessary but insufficient condition for experimental synthesis. The convex hull distance, E_{hull} , provides a more rigorous measure by comparing the energy of the $L2_1$ phase to the most stable known

phase or combination of phases at that stoichiometry. While Rh_2MnTi is the only compound in this set where the $L2_1$ structure is identified as the absolute ground state ($E_{\text{hull}} = 0$), the majority of the remaining compounds exhibit E_{hull} values below 0.200 eV/atom. This value is widely accepted as an empirical threshold, below which a material may be synthesized as a metastable phase in a specific lattice structure. Especially all Mn-based compounds have E_{hull} values very close to zero making them perfect candidates for experimental growth.

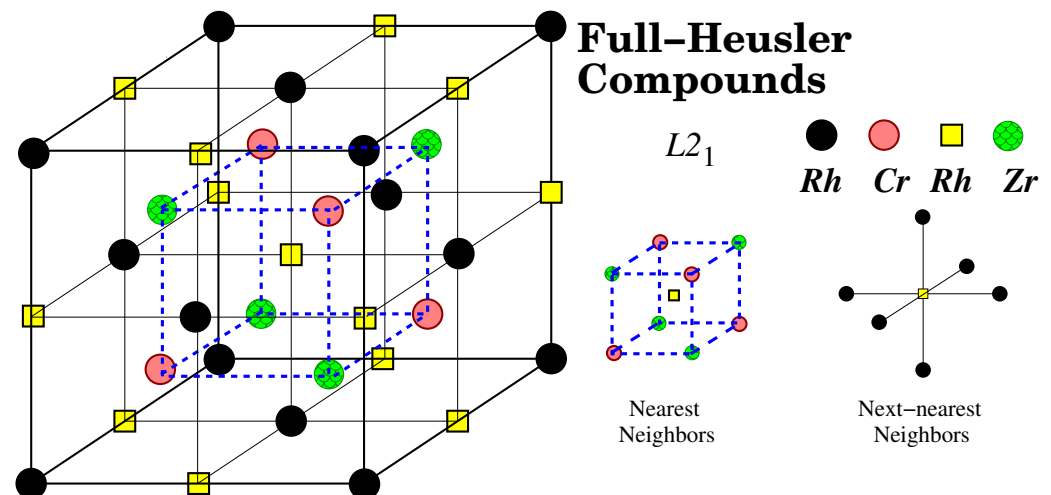


Figure 1. Schematic representation of the $L2_1$ structure adopted by the full-Heusler compounds. The black spheres, pink spheres, yellow squares, and green spheres are widely called A, B, C, and D sites, respectively. The large cube in the figure contains exactly four primitive unit cells. On the right, the nearest and next-nearest neighbors are depicted.

Table 1. For the Heusler compounds under study, we present the equilibrium lattice constant a_{eq} , the formation energy E_{form} and the energy distance from the convex hull E_{hull} (all data are taken from the Open Quantum Materials Database [48–50]).

Compound	a_{eq} (Å)	E_{form} (eV/atom)	E_{hull} (eV/atom)
Co_2VTi	5.806	−0.223	0.102
Co_2VZr	6.066	−0.087	0.200
Co_2VHf	6.001	−0.122	0.220
Co_2CrTi	5.786	−0.152	0.109
Co_2CrZr	5.983	0.180	0.421
Co_2CrHf	5.991	−0.116	0.171
Co_2MnTi	5.759	−0.289	0.010
Co_2MnZr	6.004	−0.174	0.068
Co_2MnHf	5.958	−0.250	0.037
Rh_2VTi	6.112	−0.453	0.190
Rh_2VZr	6.305	−0.362	0.282
Rh_2VHf	6.271	−0.448	0.276
Rh_2CrTi	6.078	−0.394	0.170
Rh_2CrZr	6.294	−0.390	0.183
Rh_2CrHf	6.257	−0.480	0.171
Rh_2MnTi	6.127	−0.586	0.000
Rh_2MnZr	6.352	−0.576	0.011
Rh_2MnHf	6.309	−0.662	0.011

Table 1. Cont.

Compound	a_{eq} (Å)	E_{form} (eV/atom)	E_{hull} (eV/atom)
Ir ₂ VTi	6.135	−0.479	0.234
Ir ₂ VZr	6.371	−0.350	0.368
Ir ₂ VHf	6.323	−0.445	0.322
Ir ₂ CrTi	6.143	−0.405	0.187
Ir ₂ CrZr	6.320	−0.330	0.242
Ir ₂ CrHf	6.328	−0.441	0.215
Ir ₂ MnTi	6.148	−0.578	0.032
Ir ₂ MnZr	6.379	−0.513	0.059
Ir ₂ MnHf	6.340	−0.612	0.044

3. Results and Discussion

3.1. Electronic Properties

In the initial stage of our analysis, we performed electronic band structure calculations at the equilibrium lattice constant for each compound. Figure 2 illustrates the total density of states (DOS) per formula unit (f.u.) for all Zr-containing systems, while Figure 3 presents the atom-resolved DOS for the Rh₂YZr compounds. We note that the DOS profiles remain qualitatively similar when Ti or Hf is substituted for Zr.

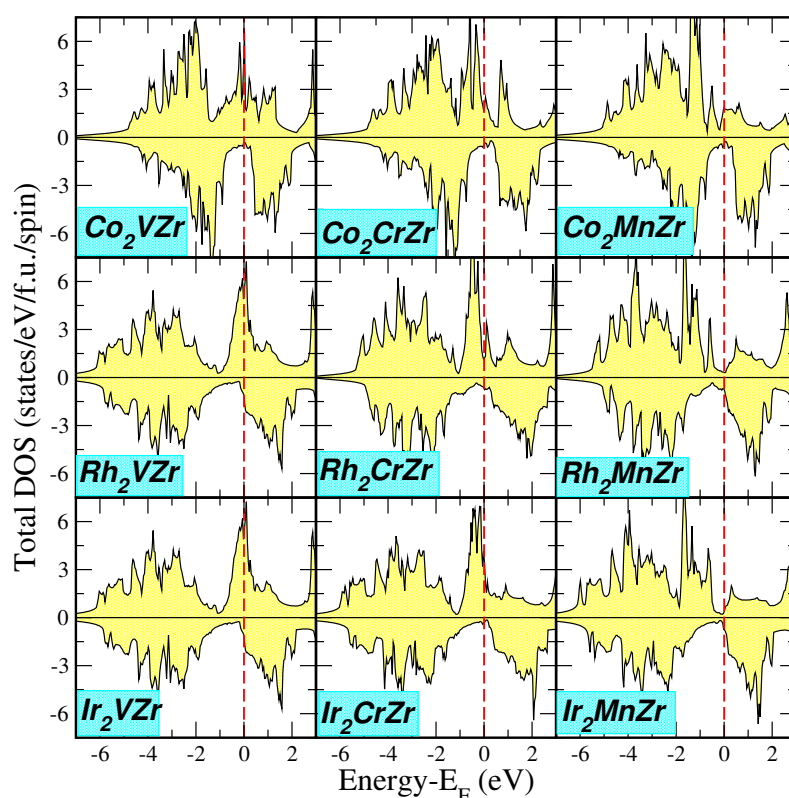


Figure 2. Total of states (DOS) for all studied Zr-based compounds assuming the $L2_1$ lattice structure. Positive (negative) DOS values correspond to the majority (minority)-spin electronic band structure. The zero energy value corresponds to the Fermi level.

The total DOS exhibits several common characteristics across the investigated series. Although not shown in the figures, a small contribution from s -states is present at low energy. The electronic structure is dominated by the d -states of the transition metal atoms, forming broad bands due to the high density of d -electrons per unit cell. For the (Co, Rh, Ir)₂YZr compounds, maintaining a constant Y element results in a consistent DOS

profile. In the minority-spin (spin-down) channel, a region of low density—referred to as a pseudogap—is consistently observed, with the Fermi level (E_F) positioned either within or slightly above this gap. When Rh replaces Co for the same Y and Z constituents, the broader $4d$ valence bands of Rh lead to less pronounced peaks and a narrowing of the minority-spin pseudogap. This trend is further intensified when Ir replaces Rh, as the even broader $5d$ bands of the Ir atoms result in a more gradual increase in the DOS surrounding the pseudogap. This behavior reveals an important distinction between the $4d$ and $5d$ substitutions. The replacement of Co by Rh already broadens the d bands and reduces the sharpness of the minority-spin pseudogap, whereas the subsequent replacement of Rh by Ir further enhances this delocalization effect. However, no new minority-spin band topology is created by the $5d$ atoms: the pseudogap remains governed by the same symmetry-derived manifold of occupied minority-spin states. The role of the $5d$ orbitals is therefore primarily to smear and weaken the pseudogap through stronger orbital overlap, rather than to open a genuine half-metallic gap.

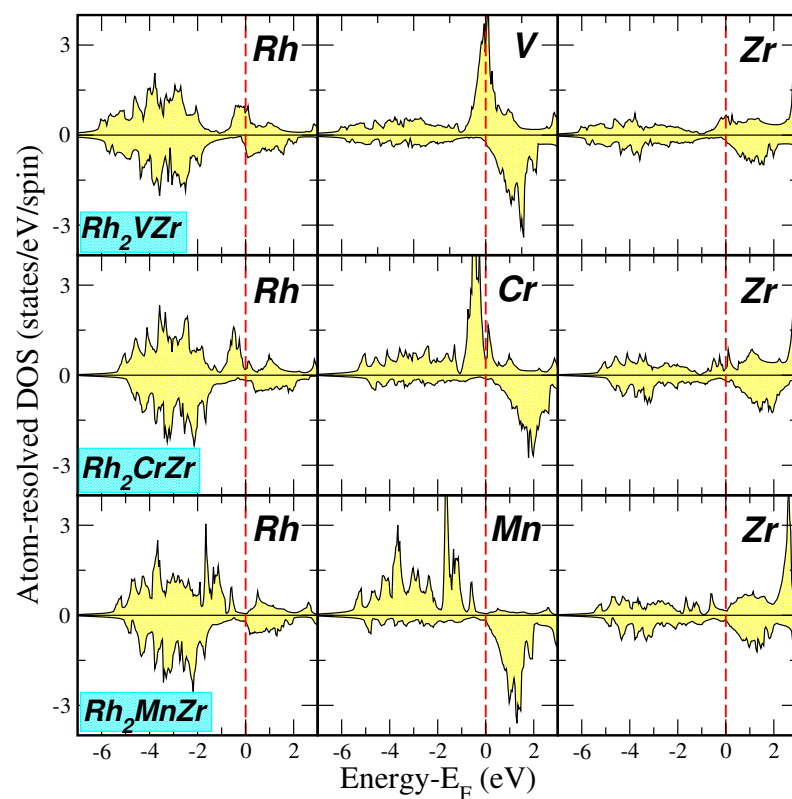


Figure 3. Similar to Figure 2 for the atom-resolved DOS in the case of $Rh_2(V,Cr,Mn)Zr$ compounds.

As shown in Figure 2, the primary variation in the total DOS occurs in the majority-spin channel near the Fermi level as the Y element progresses from V to Cr and finally to Mn. For all three $(Co, Rh, Ir)_2VZr$ compounds, E_F is pinned within a majority-spin peak. The substitution of Cr for V increases the total valence electron count by one; this extra electron is accommodated by the majority-spin band structure, which shifts the aforementioned peak to just below the Fermi level. Further substitution with Mn continues this trend, shifting E_F to even higher energies within the majority-spin channel. In contrast, the minority-spin band structure remains remarkably stable across these substitutions, showing only marginal variations.

These trends are further elucidated by the atom-resolved DOS for the $Rh_2(V, Cr, Mn)Zr$ compounds shown in Figure 3. As we move along the $3d$ transition metal series ($Y = V \rightarrow Cr \rightarrow Mn$), the Fermi level shifts toward higher energies to accommodate the increasing

valence electron count in the majority-spin states. Notably, the 3d minority-spin states of the V, Cr, and Mn atoms remain almost entirely unoccupied. The behavior of these Y-site atoms is reflected in the Rh states through hybridization; since each Y atom is surrounded by eight Rh nearest neighbors (see Figure 1), their electronic environments are strongly coupled. Finally, the Zr atoms, characterized by a low number of 4d valence electrons, contribute broad, low-intensity occupied d-bands in both spin directions.

3.2. Magnetic Properties

The calculated atomic and total spin magnetic moments for the entire series are compiled in Table 2. For the (Rh, Ir)₂YZ compounds, the substitution of Zr or Hf for Ti results in only marginal changes to both the total and atomic spin magnetic moments, indicating that the heavier Z-site elements have a negligible impact on the overall magnetic order in these specific systems. In contrast, for the Co₂YZ series, the substitution of Zr or Hf for Ti leads to an increase in the total spin magnetic moment of approximately 0.2 μ_B . This enhancement is attributed almost exclusively to the increase in the Y atomic moments.

Table 2. We present the atom resolved and total (per formula unit) spin magnetic moments for the compounds under study calculated in μ_B . The last column presents the total number of valence electrons in the primitive unit cell which contains exactly one formula unit.

Compound	$m^{\text{Co,Rh,Ir}}$	$m^{\text{V,Cr,Mn}}$	$m^{\text{Ti,Zr,Hf}}$	$m^{\text{f.u.}}$	Z_t
Co ₂ VTi	1.02	0.83	−0.05	2.81	27
Co ₂ VZr	1.01	1.15	−0.12	3.06	
Co ₂ VHf	0.99	1.14	−0.11	3.01	
Co ₂ CrTi	0.99	2.38	−0.32	4.04	28
Co ₂ CrZr	0.89	2.73	−0.25	4.26	
Co ₂ CrHf	0.88	2.72	−0.26	4.22	
Co ₂ MnTi	1.05	3.23	−0.45	4.87	29
Co ₂ MnZr	0.98	3.47	−0.37	5.07	
Co ₂ MnHf	0.98	3.43	−0.35	5.03	
Rh ₂ VTi	0.22	1.70	0.27	2.41	27
Rh ₂ VZr	0.19	2.04	0.08	2.50	
Rh ₂ VHf	0.21	2.05	0.06	2.42	
Rh ₂ CrTi	0.28	3.33	0.05	3.94	28
Rh ₂ CrZr	0.24	3.59	−0.01	4.06	
Rh ₂ CrHf	0.25	3.57	−0.03	4.04	
Rh ₂ MnTi	0.33	4.07	0.05	4.78	29
Rh ₂ MnZr	0.28	4.20	−0.03	4.72	
Rh ₂ MnHf	0.28	4.17	−0.03	4.71	
Ir ₂ VTi	0.31	1.56	0.34	2.53	27
Ir ₂ VZr	0.29	1.98	0.11	2.66	
Ir ₂ VHf	0.30	1.97	0.07	2.65	
Ir ₂ CrTi	0.24	3.24	0.27	3.98	28
Ir ₂ CrZr	0.28	3.44	0.05	4.05	
Ir ₂ CrHf	0.29	3.45	+0.00	4.04	
Ir ₂ MnTi	0.35	3.99	0.17	4.86	29
Ir ₂ MnZr	0.33	4.16	0.06	4.88	
Ir ₂ MnHf	0.34	4.14	0.05	4.87	

A more significant trend is observed when Rh or Ir is substituted for Co while keeping the Y and Z constituents constant. As illustrated in Figure 4, which depicts the evolution of the total spin magnetic moments as a function of the Y element, the total moments do not exhibit drastic variations, with the Y = V compounds showing the largest discrepancies. However, the distribution of these moments among the constituent atoms changes

substantially. Unlike Co, which typically carries a significant spin magnetic moment of approximately $1 \mu_B$, the Rh and Ir atoms—possessing $4d$ and $5d$ valence electrons, respectively—contribute much smaller fractions to the total magnetization. To compensate for the diminished X-site moment when transitioning from Co to Rh or Ir, the spin magnetic moments of the Y atoms (V, Cr, or Mn) increase considerably. This redistribution of the spin magnetic moments among the Co (Rh, Ir) and the V (Cr, Mn) atoms arises from the interplay between exchange splitting and band filling. Upon substituting Rh or Ir for Co, the former elements exhibit a considerably smaller exchange splitting of their valence d -bands, and consequently smaller spin magnetic moments. The minority-spin electronic bands then acquire a larger Rh (Ir) contribution, reducing the V (Cr, Mn) characteristics in these bands compared with the Co-based compounds. As a result, the exchange splitting of the V (Cr, Mn) valence d -bands increases, leading to larger atomic spin magnetic moments on these atoms. Simultaneously, the Ti (Zr, Hf) atoms also exhibit an increase in their induced spin magnetic moments, following the magnetic behavior of the $3d$ transition metal at the Y site. Although these Z-site moments are one to two orders of magnitude smaller than those of the V, Cr, or Mn atoms, their orientation and magnitude remain coupled to the magnetic state of the Y sublattice through hybridization effects.

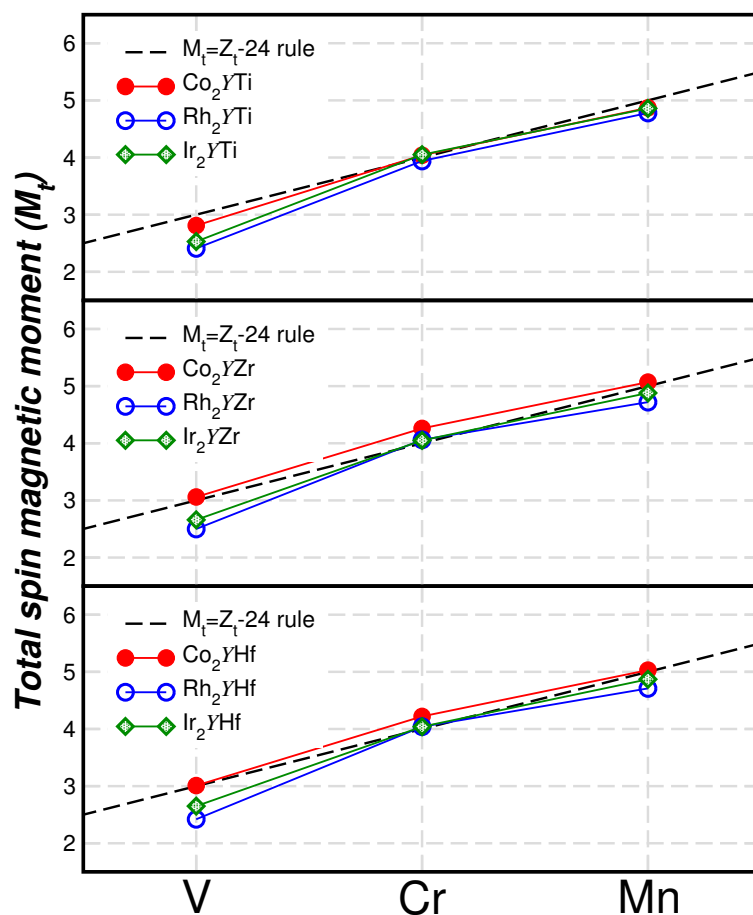


Figure 4. Ab initio calculated total spin magnetic moments, M_t , in μ_B per formula unit, for the studied compounds at their equilibrium lattice constant assuming the $L2_1$ lattice structure. The dashed line represents the $M_t = Z_t - 24$ Slater–Pauling rule where Z_t is the total number of valence electrons in the primitive unit cell.

The Ir-based compounds are particularly useful for isolating the magnetic consequence of $5d$ -orbital delocalization. Despite the presence of heavier atoms, the Ir sites do not develop large local spin magnetic moments. Instead, their extended $5d$ orbitals favor stronger hybridization with the neighboring Y-site atoms, leading to a substantial transfer

of magnetic polarization toward the V, Cr, and Mn sublattices. This effect is already visible for Rh-based systems but becomes more systematic when Ir is introduced. Consequently, the 5d substitution does not produce a new type of magnetic ordering; rather, it amplifies the sublattice-resolved moment redistribution that begins with the 4d elements.

3.3. Slater–Pauling Like Behavior

As demonstrated in the preceding discussion of spin magnetic moments, the compounds under study generally adhere to the Slater–Pauling rule, as defined in Reference [41]. The most notable discrepancies are observed for the (Rh, Ir)₂V(Ti, Zr, Hf) systems (see Figure 4). In these specific alloys, the absence of a true half-metallic gap is evident, as the Fermi level consistently intersects a minority-spin energy band. When the total spin magnetic moment (M_t) approaches an integer value, it typically follows the relation $M_t = Z_t - 24$, where Z_t represents the total number of valence electrons per formula unit. This rule effectively links the electronic and magnetic profiles of ideal half-metals by assuming the presence of exactly 12 fully occupied minority-spin bands.

To elucidate the origin of the pseudogap in these all-*d* systems, we performed an analysis similar to that presented in Reference [41]. Figure 5 displays the spin-resolved band structure for Rh₂CrZr as a prototype. The defining feature of the minority-spin channel (indicated by red lines) is the behavior of the bands at the Γ point, where their degeneracy and characteristics directly reflect the symmetry of the atomic orbitals in real space. By accounting for the degeneracy at Γ , we identify exactly twelve bands below or near the Fermi level, providing a physical basis for the observed Slater–Pauling behavior. The lack of a genuine gap—and thus the absence of true half-metallicity—stems from the complexity of the band dispersions away from the Γ point, where band crossings result in a pseudogap rather than a pristine energy void.

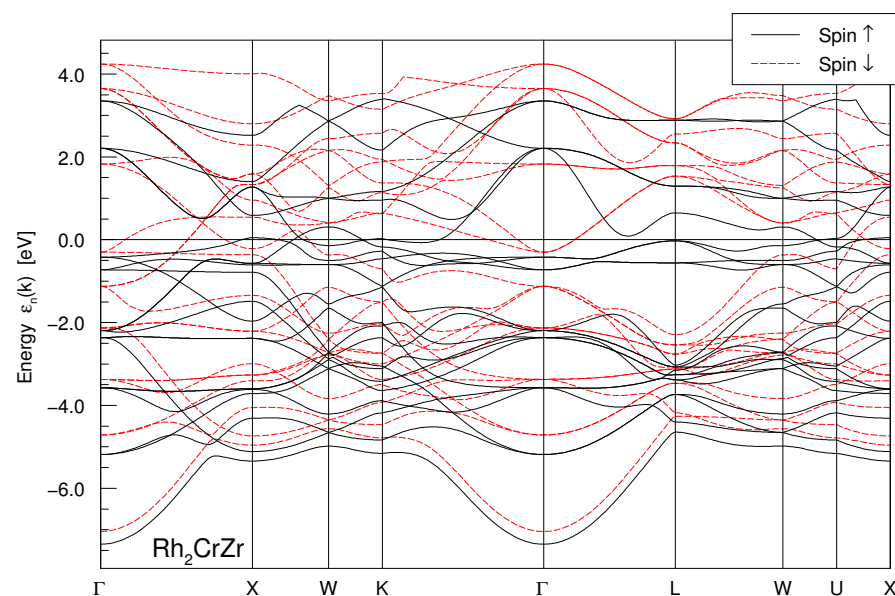


Figure 5. Spin-resolved band structure of Rh₂CrZr for several high symmetry directions in the first Brillouin zone.

The nature of these minority-spin states was further investigated using “fat band” analysis. Figure 6 schematically illustrates the characteristics of the occupied minority-spin bands for Rh₂CrZr, specifying the band degeneracies at the Γ point and the atomic orbitals contributing to each state. Similar to traditional full-Heusler alloys [7], the *d*-orbitals split according to the crystal symmetry. The overall tetrahedral (T_h) symmetry of the lattice

results in “gerade” e_g and t_{2g} states that are delocalized across the crystal. Additionally, the Rh atoms form a cubic sublattice that supports “ungerade” states (e_u and t_{1u}) consistent with octahedral (O_h) symmetry; these states are localized either on the Rh-Rh or Cr-Zr sites. As shown in Figure 6, the occupied and unoccupied d -bands overlap away from the high-symmetry Γ point. Consequently, the Fermi level intersects these states, leading to the small deviations from the ideal integer values predicted by the $M_t = Z_t - 24$ rule.

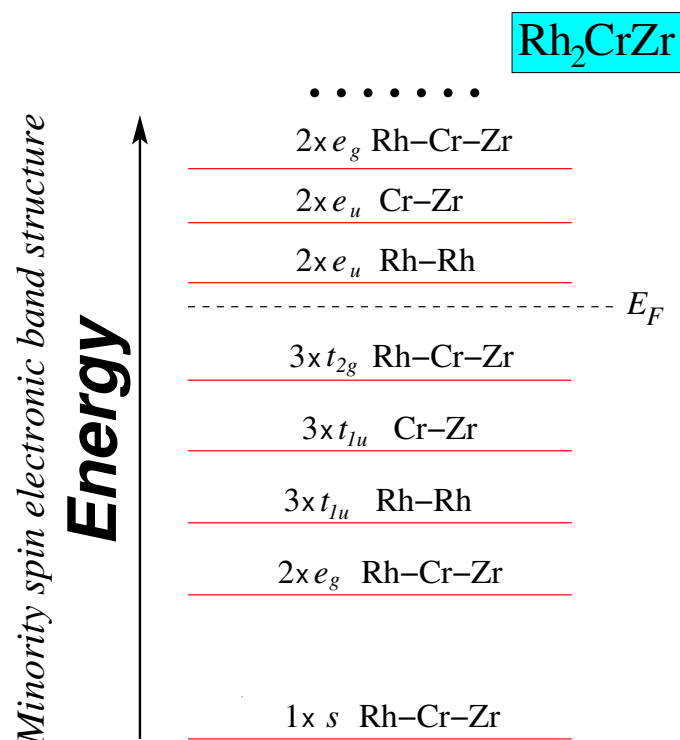


Figure 6. Schematic representation of the characteristics of the bands at the Γ point in the minority-spin band structure of Rh_2CrZr compound. Note that below the Fermi level, there are exactly 12 orbitals. Numbers indicate the degeneracy of each state.

4. Summary and Conclusions

In summary, we performed a comprehensive first-principles investigation into the structural, electronic, and magnetic properties of the all- d -metal Heusler family (Co , Rh , Ir)₂(V , Cr , Mn)(Ti , Zr , Hf). By systematically substituting transition metals across the $3d$, $4d$, and $5d$ rows, we established clear trends in their fundamental physical behavior.

First, evaluating their thermodynamic stability using formation energies and convex hull distances retrieved from the Open Quantum Materials Database (OQMD) [48–50] indicated that while most compounds are theoretically metastable in the $L2_1$ lattice structure ($E_{\text{hull}} < 0.200$ eV/atom), Rh_2MnTi stands out as a stable absolute ground state.

Electronically, these compounds are characterized by a pronounced pseudogap in the minority-spin channel. The substitution of Co with the heavier Rh and Ir atoms broadens the valence bands, which alters the shape of the pseudogap and enhances orbital hybridization.

Magnetically, the total spin magnetic moments generally adhere to the $M_t = Z_t - 24$ Slater–Pauling rule. Detailed band structure and symmetry analyses confirmed the presence of exactly 12 occupied minority-spin bands at the Γ point. All Mn -based compounds have E_{hull} values very close to zero, present a pseudogap in the minority-spin band structure and possess very large values of total spin magnetic moments, making them suitable candidates for future spintronic and magneto-electronic applications.

A central outcome of the present study, compared with previous investigations of all- $3d$ and selected $4d/5d$ all- d -metal Heusler compounds, is that the inclusion of $5d$ elements does not introduce a fundamentally new Slater–Pauling mechanism or a true half-metallic gap. The minority-spin electronic structure remains controlled by the presence of twelve occupied bands at the Γ point, while band crossings away from Γ prevent the formation of a genuine gap and lead instead to a pseudogap. In this respect, the $5d$ systems preserve the same basic symmetry mechanism found in the lighter analogues.

The essential difference introduced by the $5d$ elements is quantitative but physically important. The more spatially extended Ir $5d$ orbitals broaden the d -derived bands, increase orbital hybridization, and make the minority-spin pseudogap less sharply defined than in the Co- and Rh-based compounds. At the same time, the Ir atoms carry only small local spin moments, and the magnetization is redistributed toward the Y-site atoms. Thus, the $5d$ substitution mainly amplifies the trends initiated by $4d$ elements rather than producing an entirely new electronic phase.

These findings clarify the role of heavy transition metals in all- d -metal Heusler alloys: $5d$ chemistry should be viewed as a tuning tool for controlling band broadening, pseudogap robustness, and sublattice-resolved magnetization. This distinction from our earlier studies provides a clearer design principle for future theoretical and experimental searches, namely that high spin polarization in all- d -metal Heuslers can be optimized not only by electron counting and Slater–Pauling behavior, but also by controlling the degree of d -orbital delocalization through the choice of $4d$ and $5d$ constituents.

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Conflicts of Interest: The author declares no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

DOS	Density of states
f.u.	Formula unit
FPLO	Full-potential nonorthogonal local-orbital minimum-basis band structure approach
GGA	Generalized gradient approximation
PBE	Perdew–Burke–Ernzerhof

References

1. Heusler, F. Über magnetische manganlegierungen. *Verh. Dtsch. Phys. Ges.* **1903**, *12*, 219.
2. Heusler, F.; Take, E. The nature of the Heusler alloys. *Phys. Z.* **1912**, *13*, 897.
3. Webster, P.J.; Ziebeck, K.R.A. Alloys and Compounds of d -Elements with Main Group Elements. Part 2. In *Landolt-Börnstein, New Series, Group III*; Wijn, H.R.J., Ed.; Springer: Berlin/Heidelberg, Germany, 1988; Volume 19c, pp. 75–184.
4. Ziebeck, K.R.A.; Neumann, K.-U. Magnetic Properties of Metals. In *Landolt-Börnstein, New Series, Group III*; Wijn, H.R.J., Ed.; Springer: Berlin/Heidelberg, Germany, 2001; Volume 32/c, pp. 64–414.
5. Graf, T.; Felser, C.; Parkin, S.S.P. Simple rules for the understanding of Heusler compounds. *Prog. Solid State Chem.* **2011**, *39*, 1. [[CrossRef](#)]
6. Katsnelson, M.I.; Irkhin, V.Y.; Chioncel, L.; Lichtenstein, A.I.; de Groot, R.A. Half-metallic ferromagnets: From band structure to many-body effects. *Rev. Mod. Phys.* **2008**, *80*, 315. [[CrossRef](#)]
7. Galanakis, I. Slater–Pauling Behavior in Half-Metallic Heusler Compounds. *Nanomaterials* **2023**, *13*, 2010. [[CrossRef](#)] [[PubMed](#)]
8. Hirohata, A.; Takanashi, K. Perspectives of Heusler compounds. *J. Phys. D Appl. Phys.* **2014**, *47*, 193001. [[CrossRef](#)]
9. Galanakis, I.; Dederichs, P.H. (Eds.) Half-metallic Alloys. Fundamentals and Applications. In *Lecture Notes in Physics*; Springer: Berlin/Heidelberg, Germany, 2005; Volume 676.
10. Felser, C.; Fecher, G.H. (Eds.) *Spintronics: From Materials to Devices*; Springer: Berlin/Heidelberg, Germany, 2013.

11. Fong, C.Y.; Pask, J.E.; Yang, L.H. (Eds.) Half-metallic Materials and Their Properties. In *Series on Materials for Engineering*; Imperial College Press: London, UK, 2013; Volume 2.
12. Heusler Alloys. Properties, Growth, Applications. In *Springer Series in Materials Science*; Felser, C., Hirohata, A., Eds.; Springer International Publishing: Berlin/Heidelberg, Germany, 2018; Volume 222.
13. Gillessen, M.; Dronskowski, R. A combinatorial study of full Heusler alloys by first-principles computational methods. *J. Comput. Chem.* **2009**, *30*, 1290. [[PubMed](#)]
14. Gillessen, M.; Dronskowski, R. A combinatorial study of inverse Heusler alloys by first-principles computational methods. *J. Comput. Chem.* **2010**, *31*, 612. [[PubMed](#)]
15. Ma, J.; Hegde, V.I.; Munira, K.; Xie, Y.; Keshavarz, S.; Mildebrath, D.T.; Wolverton, C.; Ghosh, A.W.; Butler, W.H. Computational investigation of half-Heusler compounds for spintronics applications. *Phys. Rev. B* **2017**, *95*, 024411. [[CrossRef](#)]
16. Ma, J.; He, J.; Mazumdar, D.; Munira, K.; Keshavarz, S.; Lovorn, T.; Wolverton, C.; Ghosh, A.W.; Butler, W.H. Computational investigation of inverse Heusler compounds for spintronics applications. *Phys. Rev. B* **2018**, *98*, 094410. [[CrossRef](#)]
17. Sanvito, S.; Oses, C.; Xue, J.; Tiwari, A.; Zic, M.; Archer, T.; Tozman, P.; Venkatesan, M.; Coey, M.; Curtarolo, S. Accelerated discovery of new magnets in the Heusler alloy family. *Sci. Adv.* **2017**, *3*, e1602241. [[CrossRef](#)] [[PubMed](#)]
18. Faleev, S.V.; Ferrante, Y.; Jeong, J.; Samant, M.G.; Jones, B.; Parkin, S.S.P. Unified explanation of chemical ordering, the Slater–Pauling rule, and half-metallicity in full Heusler compounds. *Phys. Rev. B* **2017**, *95*, 045140. [[CrossRef](#)]
19. Faleev, S.V.; Ferrante, Y.; Jeong, J.; Samant, M.G.; Jones, B.; Parkin, S.S.P. Origin of the Tetragonal Ground State of Heusler Compounds. *Phys. Rev. Appl.* **2017**, *7*, 034022. [[CrossRef](#)]
20. Faleev, S.V.; Ferrante, Y.; Jeong, J.; Samant, M.G.; Jones, B.; Parkin, S.S.P. Heusler compounds with perpendicular magnetic anisotropy and large tunneling magnetoresistance. *Phys. Rev. Mater.* **2017**, *1*, 024402. [[CrossRef](#)]
21. Oliynyk, A.O.; Antono, E.; Sparks, T.D.; Ghadbeigi, L.; Gaultois, M.W.; Meredig, B.; Mar, A. High-Throughput Machine-Learning-Driven Synthesis of Full-Heusler Compounds. *Chem. Mater.* **2016**, *28*, 7324. [[CrossRef](#)]
22. Wei, Z.Y.; Liu, E.K.; Li, Y.; Han, X.L.; Du, Z.W.; Luo, H.Z.; Liu, G.D.; Xi, X.K.; Zhang, H.W.; Wang, W.H.; et al. Magnetostructural martensitic transformations with large volume changes and magneto-strains in all-d-metal Heusler alloys. *Appl. Phys. Lett.* **2016**, *109*, 071904. [[CrossRef](#)]
23. Wei, Z.Y.; Liu, E.K.; Chen, J.H.; Li, Y.; Liu, G.D.; Luo, H.Z.; Xi, X.K.; Zhang, H.W.; Wang, W.H.; Wu, G.H. Realization of multifunctional shape-memory ferromagnets in all-d-metal Heusler phases. *Appl. Phys. Lett.* **2015**, *107*, 022406. [[CrossRef](#)]
24. Ni, Z.; Ma, Y.; Liu, X.; Luo, H.; Liu, H.; Meng, F. Electronic structure, magnetic properties and martensitic transformation in all-d-metal Heusler alloys Zn_2YMn ($\text{Y} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$). *J. Magn. Magn. Mater.* **2018**, *451*, 721. [[CrossRef](#)]
25. Ni, Z.; Guo, X.; Liu, X.; Jiao, Y.; Meng, F.; Luo, H. Understanding the magnetic structural transition in all-d-metal Heusler alloy $\text{Mn}_2\text{Ni}_{1.25}\text{Co}_{0.25}\text{Ti}_{0.5}$. *J. Alloys Compd.* **2019**, *775*, 427. [[CrossRef](#)]
26. Samanta, S.; Ghosh, S.; Mandal, K. Observation of giant exchange bias effect in Ni–Mn–Ti all-d-metal Heusler alloy. *J. Phys. Condens. Matter* **2022**, *34*, 105801.
27. Aznar, A.; Gràcia-Condal, A.; Planes, A.; Lloveras, P.; Barrio, M.; Tamarit, J.-L.; Xiong, W.; Cong, D.; Popescu, C.; Manosa, L. Giant barocaloric effect in all-d-metal Heusler shape memory alloys. *Phys. Rev. Mater.* **2019**, *3*, 044406. [[CrossRef](#)]
28. Samanta, S.; Ghosh, S.; Chatterjee, S.; Mandal, K. Large magnetocaloric effect and magnetoresistance in Fe-Co doped $\text{Ni}_{50-x}(\text{FeCo})_x\text{Mn}_{37}\text{Ti}_{13}$ all-d-metal Heusler alloys. *J. Alloys Compd.* **2022**, *910*, 164929. [[CrossRef](#)]
29. Samanta, S.; Chatterjee, S.; Ghosh, S.; Mandal, K. Large reversible magnetocaloric effect and magnetoresistance by improving crystallographic compatibility condition in Ni(Co)-Mn-Ti all-d-metal Heusler alloys. *Phys. Rev. Mater.* **2022**, *6*, 094411. [[CrossRef](#)]
30. Shen, J.; Zeng, Q.; Zhang, H.; Xi, X.; Liu, E.; Wang, W.; Wu, G. Atomic configuration, unusual lattice constant change, and tunable ferromagnetism in all-d-metal Heusler alloys $\text{Fe}_2\text{CrV-FeCr}_2\text{V}$. *J. Magn. Magn. Mater.* **2019**, *492*, 165661. [[CrossRef](#)]
31. Mert, G. Magnetic phase transitions of all-d metal Heusler type model. *J. Alloys Compd.* **2020**, *819*, 153299. [[CrossRef](#)]
32. Tanzim, M.F.; Fortunato, N.; Samathrakris, I.; Xie, R.; Opahle, I.; Gutfleisch, O.; Zhang, H. Giant Anomalous Hall and Nernst Conductivities in Magnetic All-d Metal Heusler Alloys. *Adv. Funct. Mater.* **2023**, *33*, 2214967. [[CrossRef](#)]
33. de Paula, V.G.; Reis, M.S. All-d-Metal Full Heusler Alloys: A Novel Class of Functional Materials. *Chem. Mater.* **2021**, *33*, 5483. [[CrossRef](#)]
34. Marathe, M.; Herper, H.C. Exploration of all-3d Heusler alloys for permanent magnets: An ab initio based high-throughput study. *Phys. Rev. B* **2023**, *107*, 174402. [[CrossRef](#)]
35. Nia, S.; Khenchoul, S.; Lefkaier, I.K.; Lagoun, B. DFT-based investigation of the structural, magnetic, electronic, half-metallicity and elastic properties in the all-d Heusler compounds: The case of Co_2VZn and CoVZn . *Eur. Phys. J. B* **2021**, *94*, 118. [[CrossRef](#)]
36. Jin, T.; Jung, Y. Classifying Intermetallic Tetragonal Phase of All-d-Metal Heusler Alloys for Catalysis Applications. *Top. Catal.* **2022**, *65*, 208.
37. Zeng, Q.; Shen, J.; Zhang, H.; Chen, J.; Ding, B.; Xi, X.; Liu, E.; Wang, W.; Wu, G. Electronic behaviors during martensitic transformations in all-d-metal Heusler alloys. *J. Phys. Condens. Matter* **2019**, *31*, 425401. [[CrossRef](#)] [[PubMed](#)]

38. Fortunato, N.M.; Taubel, A.; Marmodoro, A.; Pfeuffer, L.; Opahle, I.; Ebert, H.; Gutfleisch, O.; Zhang, H. High-Throughput Design of Magnetocaloric Materials for Energy Applications: MMX alloys. *Adv. Sci.* **2023**, *10*, 2206772. [CrossRef]
39. Fortunato, N.M.; Li, X.; Schöpnecker, S.; Xie, R.; Taubel, A.; Scheibel, F.; Opahle, I.; Gutfleisch, O.; Zhang, H. High-Throughput Screening of All-d-Metal Heusler Alloys for Magnetocaloric Applications. *Chem. Mater.* **2024**, *3*, 6765. [CrossRef]
40. Özdoğan, K.; Maznichenko, I.V.; Ostanin, S.; Şaşıoğlu, E.; Ernst, A.; Mertig, I.; Galanakis, I. High spin polarization in all-3d-metallic Heusler compounds: The case of Fe_2CrZ and Co_2CrZ ($Z = \text{Sc, Ti, V}$). *J. Phys. D Appl. Phys.* **2019**, *52*, 205003. Corrigendum in *J. Phys. D Appl. Phys.* **2024**, *57*, 049501. [CrossRef]
41. Tas, M.; Özdoğan, K.; Şaşıoğlu, E.; Galanakis, I. High Spin Magnetic Moments in All-3d-Metallic Co-Based Full Heusler Compounds. *Materials* **2023**, *16*, 7543. [CrossRef]
42. Tas, M.; Şaşıoğlu, E.; Galanakis, I. Magnetic Properties of All-d Metallic Heusler Compounds: A First-Principles Study. *Magnetism* **2024**, *4*, 400. [CrossRef]
43. Koepnick, K.; Eschrig, H. Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme. *Phys. Rev. B* **1999**, *59*, 1743. [CrossRef]
44. Koepnick, K. Full Potential Local Orbital Minimum Basis Bandstructure Scheme User's Manual. Available online: <http://www.fplo.de/download/doc.pdf> (accessed on 10 May 2026).
45. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865. [CrossRef] [PubMed]
46. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188. [CrossRef]
47. Kandpal, H.C.; Fecher, G.H.; Felser, C.; Schönhense, G. Correlation in the transition-metal-based Heusler compounds Co_2MnSi and Co_2FeSi . *Phys. Rev. B* **2006**, *73*, 094422. [CrossRef]
48. Available online: <https://oqmd.org> (accessed on 15 May 2026).
49. Saal, J.E.; Kirklin, S.; Aykol, M.; Meredig, B.; Wolverton, C. Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Materials Database (OQMD). *JOM* **2013**, *65*, 1501. [CrossRef]
50. Kirklin, S.; Saal, J.E.; Meredig, B.; Thompson, A.; Doak, J.W.; Aykol, M.; Rühl, S.; Wolverton, C. The Open Quantum Materials Database (OQMD): Assessing the accuracy of DFT formation energies. *npj Comput. Mater.* **2015**, *1*, 15010. [CrossRef]

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