Structural, electronic, and magnetic properties of Heusler X_2MnZ with X=Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt, Au and Z=Al, Si, Ga, Ge, In and Sn: A systematic density functional theory investigation.

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Abstract

An exhaustive study of the structural stability, electronic, and magnetic properties of the ternary X_2MnZ Heusler alloys, in cubic and tetragonal lattice cells, is presented. We performed density-functional-theory (DFT) calculations, as implemented in the SIESTA code, for X=Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt, and Au, and Z=Al, Si, Ga, Ge, In, and Sn. The spin polarized local electronic density of states for the different chemical components in the various alloys are calculated and the some particular examples are discussed. From those results we observe that the candidates for semi-metallic behaviour are Fe_2MnSi, Co_2MnSi, Co_2MnGe and Ru_2MnGe. A general feature is that Mn donates of the order of one electron to the other components. We calculated the magnetic moment per unit cell and the individual contributions coming from the other elements, and observe the change as a function of X and Z. The largest moment per unit cell corresponds to Fe_2MnIn (7.86 μ_B) and the smallest to Ru_2MnIn (2.15 μ_B). The crystalline structure, as well of the lattice parameter are discussed. We compare with the existing experimental data and find a fair agreement.

Keywords: Structure, electronic, and magnetic properties of Heusler alloys, DFT calculations,

INTRODUCTION

Heusler alloys (HA) are some of the most interesting magnetic systems. They are ternary alloys with a chemical formula X_2MnZ, that crystallize with a $L2_1$ structure.[**?** **?** **?**] This structure can be described by four interpenetrating *fcc* sublattices; two of them occupied by the X atoms, and the other two by Mn and Z elements. In general, the X element is a transition or noble metal and Z is one element of the IIIA (Al, Ga, In), IVA (Si, Ge, Sn) or VA (Sb) columns of the periodic table.

As can be observed in Figure 1, in the structural ground state, the Mn atoms (purple circles) are surrounded by eight first neighbors of type X (pink circles) and six second neighbors of type Z (light brawn circles). Thus, the shortest Mn-Mn pair occurs at the third neighbor shell. Due to the large distance between Mn atoms it is believed that the magnetic coupling is via the itinerant electrons of the X and Mn atoms. At finite temperatures, when the atoms exchange lattice sites, the magnetic interactions, sign and magnitude, will be determined by the amount of spatial disorder present in the system i.e., how many first, second and third Mn neighbors pairs are present in the system.

In all the HA, Mn plays an important role and depending on the chemical composition and the atomic order, they can be ferromagnets, ferrimagnets, antiferromagnets of various types, or helicoidal. In the case in which the X component is non-magnetic the magnetic moment is mainly localized in the Mn atom and can be as high as 4.3 μ_B ($Pd2_2MnIn$).[**?**] On the other hand, if X is magnetic, both magnetic elements can give rise to 5.11 μ_B (Co_2MnGe).[**?**] Furthermore, they have very high Curie temperatures that can be as high as 985 K (Co_2MnSi).[**?**]

As a function of temperature, the three chemical spices exchange lattice sites and produce a rich variety of atomic disordered systems that influence the magnetic properties. These alloys present a great opportunity to understand the interplay between magnetism and atomic order.[**?** **?**]. In addition, in some systems, like Ni-Mn-Ga, the coupling between structure and magnetism, induce martensitic transformations that bring interesting magnetic shape-memory and magnetic superelasticity properties.[**?**].

One more property that makes these systems subject of intensive research is that some are half-metallic. There is a gap in the spin down sub-band at the Fermi level. Thus, they can be used to provide electrons with only one spin polarization; the key property for

spintronics [**?** **?**] and magnetically driven actuators[**?**].

Our interest here is to study in a systematic way the electronic, magnetic and stability properties of 60 systems; i.e. X=Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt and Au and Z = Al, Ga, In, Si, Ga, and Sn. We present in Figure 2, the periodic table showing the elements that form the X_2MnZ systems reported here: Mn, the transition metals in yellow (X element) and the IIIA and IVA column elements in green (Z element).

In Section II we present the model and computational details. In Sec. III we discuss our results; first we address the electronic structure, then we discuss the magnetic properties and give results for the magnetic properties. Finally, we report on the ground state crystalline structure. Comparison with experimental results are also given.

DETAILS OF THE COMPUTATIONAL PROCEDURE AND MODEL

Our calculations were performed using the SIESTA DFT package,[**?**] which employs numerical pseudo-atomic orbitals as basis sets to solve the single-particle Kohn-Sham equations. In this work we used the Perdew-Burke-Ernzerhof form of the generalized gradient approximation (GGA) for the exchange and correlation potential,[**?**] and the atomic cores were described by nonlocal norm-conserving scalar-relativistic Troullier-Martins pseudopotentials,[**?**] factorized in the Kleinman-Bylander form.[**?**] The pseudo-potentials for all the different elements studied here, were generated using the valence configurations. More details on the reliability, basis sets used, and about the pertinent tests that we carried out, can be found in the literature.[**?** **?**] The valence states were described using a double-ζ doubly polarized basis set.

An electronic temperature of 25 meV for smearing, and a 250 Ry energy cutoff to define the real-space grid for numerical calculations involving the electron density was implemented. We have tested larger cutoffs and lower electronic temperatures for some particular cases, and verified that they do not modify substantially the results. To optimize the lattice constant and atomic positions we performed a local relaxation using the conjugate gradient algorithm,[**?**] starting from cubic and tetragonal basic lattice cells. The structural optimization was finalized when each force component, on each atom in the cluster, was smaller than 6 meV/Å.

All the calculations were performed assuming cubic and tetragonal (for Pd, Ag, Pt and

Au) lattice vectors with an atomic base of 16 atoms (see Figure 1) keeping the X_2MnZ stoichiometry. The binding energy E_b is defined as follows:

$$E_b(X_8Mn_4Z_4) = \frac{E_{\rm Total}(X_8Mn_4Z_4) - 8E_{\rm atom}(X) - 4E_{\rm atom}(Mn) - 4E_{\rm atom}(Z)}{16} \ ,, \qquad (1)$$

RESULTS

We calculated the electronic structure of the 60 systems; X_2MnZ with X=Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt and Au and Z = Al, Ga, In, Si, Ga, and Sn. We included in the calculation all the s, p, and d, valence electrons. Here, we present in detail the spin up and spin down local electronic density of states (SPLDS) for some representative systems, in the energy region around the Fermi energy. We show also how the total spin up and down electronic densities of states evolve as we substitute for a particular X series the Z element. The physical properties are discussed in three tables for each series X=3d, 4d, and Pt, and noble metals. First, we note how the electrons distribute in the ordered alloy and from the local electronic density of states we analyze the half-metallic behavior. Then from the spin polarized density of states we calculate the magnetic moment at each chemical component, and the total magnetic moment per unit cell. Finally we give the cohesive energy of the alloys and the equilibrium crystalline structures and lattice constants.

X_2MnZ with X = Fe, Co, Ni, and Z = Al, Ga, In, Si, Ga, and Sn

In Figure 3 we show the results for the spin polarized local density of states (SPLDS) for Co_2MnSi alloy, on each of the chemical elements. In the upper panel we present the total spin-polarized electronic density of states (black curve), and the 3d (in blue), 4s (in red), Co electronic contributions. In the central panel we show the SPLDS on the Mn sites. One sees that the 3d electron band with spin down is mostly empty, giving rise to a large magnetic moment. In the lower one the 3s (in yellow) and 3p (in green) contribution on the Si atoms are shown. As reported previously, we observe that the 3d electrons of Co and Mn are the ones that determine the magnetic properties of the system. The 4s electrons form a wide conducting band. On the other hand, the Si spectrum shows a wide 3p band partially polarized and a 3s band deep in energy. One more characteristic of this system is

TABLE I. Transferred electronic charge between the atoms of the X_2MnZ Heusler like systems with X = Fe, Co, Ni and Z= Al, Ga, In Si, Ge and Sn. In the last column we give the ratio between the electronic densities of states of opposite spins (the smaller over the larger) at the Fermi Energy.

X_2YZ	X(Charge) (e)	Mn(Charge) (e)	Z(Charge) (e)	TLDS ratio
Fe_2MnAl	0.473	-0.899	-0.048	0.16
Fe_2MnGa	0.510	-0.674	-0.346	0.21
Fe_2MnIn	1.030	-0.784	-1.276	0.58
Fe_2MnSi	1.035	-0.706	-1.365	0.00
Fe_2MnGe	0.815	-0.846	-0.784	0.65
Fe_2MnSn	1.024	-0.693	-1.354	0.22
Co_2MnAl	0.348	-0.944	0.250	0.41
Co_2MnGa	0.317	-0.723	0.090	0.43
Co_2MnIn	0.941	-0.851	-1.030	0.23
Co_2MnSi	0.705	-0.731	-0.678	0.00
Co_2MnGe	0.407	-0.949	0.136	0.06
Co_2MnSn	0.957	-0.765	-1.148	0.25
Ni_2MnAl	0.315	-1.036	0.407	0.37
Ni_2MnGa	0.177	-0.895	0.540	0.51
Ni_2MnIn	0.814	-1.024	-0.603	0.27
Ni_2MnSi	0.600	-0.859	-0.341	0.85
Ni_2MnGe	0.199	-1.063	0.664	0.34
Ni_2MnSn	0.884	-0.881	-0.886	0.74

the negligible spin-down LDS at the Fermi energy, which gives the half-metallic character of this alloy.[**?**]

In Figure 4, we show the electronic structure of the six systems Co_2MnZ; Z=Al, Ga, and In, in the upper figures and Si, Ge, and Sn, in the lower part. We see that the general characteristics around the Fermi energy prevail, but the value in the spin-down density of states is smaller for the Si, Ge, and Sn, systems. Also, a general behavior is the donation of electrons from the Mn atoms, discussed below.

In Table **??**, we summarize the electron distribution in the three atomic components of the $3d$ magnetic series. In the second to fourth columns, we give the difference between the total number of electron of each element in the atomic case minus that number when

TABLE II. The magnetic moment per unit cell (μ_B), and the magnetic moments of each of the elements in the X_2MnZ Heusler alloys. The X element is a magnetic $3d$ element, and Z = Al, Ga, In, Si, Ge, and Sn. The values in brackets and bold face are experimental data.

X_2MnZ	(Mag.Mom.)/ (per unit cell)	X(μ_B)	Mn(μ_B)	Z(μ_B)
Fe_2MnAl	6.40	2.193	2.413	-0.400
Fe_2MnGa	7.22	2.374	2.828	-0.362
Fe_2MnIn	7.86	2.428	3.134	-0.130
Fe_2MnSi	3.00 (**2.2**)[**?**]	0.081	2.828	0.010
Fe_2MnGe	4.91	1.325	2.502	-0.242
Fe_2MnSn	7.10	2.118	3.043	-0.178
Co_2MnAl	4.07 (**4.01**)[**?**]	0.612	3.066	-0.226
Co_2MnGa	4.21 (**4.05**)[**?**]	0.605	3.229	-0.230
Co_2MnIn	4.97	0.799	3.415	-0.046
Co_2MnSi	5.00 (**5.07**)[**?**]	0.893	3.253	-0.037
Co_2MnGe	5.00 (**5.11**)[**?**]	0.901	3.395	-0.196
Co_2MnSn	5.09 (**5.08**)[**?**]	0.817	3.491	-0.038
Ni_2MnAl	4.28	0.304	3.742	-0.019
Ni_2MnGa	4.33 (**4.17**)[**?**]	0.299	3.871	-0.138
Ni_2MnIn	4.45 (**4.40**)[**?**]	0.244	3.942	0.020
Ni_2MnSi	4.07	0.178	3.665	0.045
Ni_2MnGe	4.17	0.217	3.845	-0.106
Ni_2MnSn	4.29(**4.05**)[**?**]	0.176	3.897	0.036

they are alloyed. For the case of Fe series, Mn and the Z atoms donate electrons to Fe. In the Co and Ni series the behavior is similar except for Z= Al, Ga, and Ge. The magnetic elements Fe, Co, and Ni always increase their number of electrons, reducing thereby their atomic magnetic moment, as will be commented below.

To give an idea of the half-metallic behavior, we show in the last column the ratio between the values of the total electronic densities of states (SPLDS) of opposite spins at the Fermi level. The systems with very low ratio are Fe_2MnSi, Co_2MnSi and Co_2MnGe. A finite gap in the spin-down band makes these systems half-metallic and potential candidates for spin valves.

In Table **??**, we show the results for the magnetic moment per unit cell and the contri-

TABLE III. Structural properties of the X_2MnZ Heusler alloys. The X element is a magnetic $3d$ element, and Z = Al, Ga, In, Si, Ge, and Sn. The crystalline structure for all the systems is cubic. The lattice constant is given in (Å), and the binding energy in eV/atom. The values in brackets and bold face, are experimental data.

X_2MnZ	Lattice Parameter ($\AA$)	Binding Energy (eV/atom)
Fe_2MnAl	5.909	-4.288
Fe_2MnGa	6.006	-3.956
Fe_2MnIn	6.197	-3.659
Fe_2MnSi	5.651 (**5.664**)[**?**]	-4.767
Fe_2MnGe	5.789 (**5.76**)	-4.385
Fe_2MnSn	6.142	-3.990
Co_2MnAl	5.789(**5.756**)[**?**]	-4.736
Co_2MnGa	5.873(**5.770**)[**?**]	-4.347
Co_2MnIn	6.078	-3.988
Co_2MnSi	5.694(**5.654**)[**?**]	-5.080
Co_2MnGe	5.825(**5.743**)[**?**]	-4.772
Co_2MnSn	6.066(**6.000**)[**?**]	-4.382
Ni_2MnAl	5.909	-4.477
Ni_2MnGa	5.993(**5.825**)[**?**]	-4.131
Ni_2MnIn	6.162(**6.068**)[**?**]	-3.811
Ni_2MnSi	5.766	-4.664
Ni_2MnGe	5.909	-4.429
Ni_2MnSn	6.138(**6.052**)[**?**]	-4.111

butions coming from the three chemical elements. In the cases where experimental values are reported we show them in brackets and bold face. It is worth noticing that most of the experimental values are reported at high temperatures, at which there may be a considerable amount of chemical disorder. A direct comparison is not possible, since chemical disorder may modify the magnetic moments.[**?**]

The highest values are obtained for the Fe series. In this series the highest magnetic moment per unit cell is 7.86 μ_B for Fe_2MnIn. The partial contributions for Fe, Mn and In are 2.428, 3.13 and -0.130 μ_B, respectively. The lowest occurs in Fe_2MnSi; 3 μ_B per unit cell, and the partial values are 0.081, 2.828 and 0.010 μ_B for Fe, Mn, and Si, respectively. In

this case there are some experiments that report the properties in a chemically disordered state[**?**]. The authors report values of 1.35 and 2.2 μ_B, per unit cell, at 77 and 4.2 K, respectively. For comparison with the theoretical calculation, we take the value measured at the lowest temperature. It is also important to note that the coupling of Mn with the Z element, except for the case of Si, is antiferromagnetic.

The Co series is the most studied and experimental results for five out of the six cases are reported. The largest value for the magnetic moment per unit cell ($5.09\mu_B$) is obtained for Co_2MnSn which is in very good agreement with the experimental value (5.08 μ_B). In the other cases the theoretical and experimental values are in fair agreement. The Mn magnetic moment is larger than for the cases of the Fe systems and the magnetic coupling between Mn and the Z elements is antiferromagnetic in all cases.

In the Ni series the largest value for the magnetic moment per unit cell corresponds to Ni_2MnIn (4.45 μ_B), a value very similar to the one reported experimentally (4.40 μ_B). Manganese shows also the largest magnetic moment value (3.94 μ_B) of the $3d$ alloys. The other two cases reported experimentally, Ni_2MnGa and Ni_2MnSn, differ more from our ground state (zero K) calculations. For these series In, Si, and Sn couple ferromagnetically to the other two chemical elements. That is not the case of Z= Al, Ga, and Ge, whose coupling is antiferromagnetic.

In Table **??** we give the results for the lattice parameter in Å and the cohesive energy in eV. The crystalline structure for all the $3d$ alloys is cubic. In the Fe series, the smallest lattice parameter for the elements in Column IIIA, of the periodic table, corresponds to Al (5.909 Å) and the highest cohesive energy (4.288 eV). On the other hand, the largest lattice parameter of the elements in that column is attained in the In case (6.197 Å) and the smallest cohesive energy (3.659 eV). For the elements in the IVA column a similar trend is observed: the smallest and largest lattice constants and the highest and smallest cohesive energy correspond to Si and Sn. In this series the experimental value reported by Niculescu et al. [**?**] for Fe_2MnGe, differs only by 0.029 Å.

As mentioned above, the Co series is the most studied, with the exception of the In system, there are experimental results for the rest. In general the calculated values are in very good agreement with the measurement. The largest discrepancy corresponds to Co_2MnGa (0.103 Å)

The Ni Heusler alloys that have been analysed experimentally are those with Ga, In and

TABLE IV. Transferred electronic charges between the atoms of the X_2MnZ Heusler like systems with X = Ru, Rh, Pd, Pt and Z= Al, Ga, In, Si, Ge and Sn. In the last column we give the ratio between the electronic densities of states of opposite spins (the larger over the smaller).

X_2YZ	X(Charge) (e)	Mn(Charge) (e)	Z(Charge) (e)	DOS ratio
Ru_2MnAl	0.767	-1.125	-0.411	0.24
Ru_2MnGa	0.893	-0.980	-0.807	0.10
Ru_2MnIn	1.406	-0.930	-1.881	0.24
Ru_2MnSi	1.189	-0.701	-1.677	0.02
Ru_2MnGe	1.026	-1.086	-0.965	0.00
Ru_2MnSn	1.321	-0.913	-1.728	0.02
Rh_2MnAl	0.697	-1.160	-0.233	0.06
Rh_2MnGa	0.800	-1.100	-0.500	0.16
Rh_2MnIn	1.283	-1.060	-1.507	0.19
Rh_2MnSi	1.031	-0.819	-1.241	0.91
Rh_2MnGe	0.826	-1.113	-0.538	0.87
Rh_2MnSn	1.208	-0.943	-1.475	0.57
Pd_2MnAl	0.332	-1.032	0.369	0.40
Pd_2MnGa	0.358	-1.100	0.383	0.34
Pd_2MnIn	0.840	-1.081	-0.598	0.37
Pd_2MnSi	0.575	-0.915	-0.233	0.62
Pd_2MnGe	0.226	-1.069	0.619	0.74
Pd_2MnSn	0.816	-0.906	-0.726	0.39
Pt_2MnAl	0.354	-1.156	0.448	0.54
Pt_2MnGa	0.433	-1.175	0.310	0.73
Pt_2MnIn	0.971	-1.182	-0.761	0.71
Pt_2MnSi	0.610	-0.940	-0.281	0.69
Pt_2MnGe	0.338	-1.119	0.443	0.76
Pt_2MnSn	0.944	-1.010	-0.880	0.95

Sn. The calculated (experimental) values for the lattice constants, all in angstroms, are 5.993 (5.825), 6.162 (6.008), 6.138 (6.052), respectively.

X_2MnZ with X = Ru, Rh, Pd, Pt, and Z = Al, Ga, In, Si, Ga, and Sn

Now we consider the series of $4d$ elements and Pt $5d$. In Figure 5 we show the results for the spin polarized local density of states (SPLDS) for the Rh_2MnGe alloy, on each of the chemical elements, with $L2_1$ crystallographic structure. It is worth noticing that the vertical scale is different in the three panels. In the upper panel we present the total SPLDS (black curve), and the $4d$ (in purple) Rh electronic contribution. In this case the band spin splitting is small and one expects a reduced magnetic moment. In the central panel we show the SPLDS on the Mn sites. One sees that the $3d$ electron band with spin down is mostly empty, giving rise to an important contribution to the alloy magnetic moment. In the lower figure, the Ge electronic contribution is presented; the $4s$ and $3d$ bands are completely full and deeper in energy. The only valence electrons are the $4p$ (in green) states.

As mentioned above the $4d$ Rh band appears with similar occupation of spin-up and spin-down and observe that the $3d$ electrons of Mn are the ones that determine the magnetic properties of the system. The $4s$ electrons form a wide conducting band. On the other hand, the Ge spectrum shows a wide $4p$ band partially polarized.

In Figure 6 we show how the electronic structure changes as the Z element goes from Al to In (Group IIIA) and from Si to Sn (Group IVA). The spin-down band bellow the Fermi energy is mainly produced by the X element whereas the spin-down band above the Fermi energy comes from the $3d$ Mn electrons. One further observation is that the gap in the spin-down band observed for X=Co and the Z=Si, Ge and Sn is not present in these series. A similar behavior is obtained for X=Ru, Pd, and Pt

In Table **??**, we summarize the electron distribution in the three atomic components of the $4d$ magnetic series and the $5d$ Pt. In the second to fourth columns, we give the difference between the total number of electrons of each element in the atomic case minus that number when they are alloyed. In all the cases, electrons are transferred to the X elements (Ru, Rh, Pd, and Pt). Mn donates electrons as much as 1.182, in the case of Pt_2MnIn, but in most of the cases the transfer is about 1 electron. The Z element acts also as a donor for the Ru and Rh. In the other two series (Pd and Pt) in the cases of X=Al, Ga, and Ge behave as an acceptor of electrons and for X=In, Si, and Sn they are donors.

To give an idea of the half-metallic behavior, we show in the last column the ratio between the values of the total electronic densities of states with opposite spins at the Fermi level.

TABLE V. Magnetic moment per unit cell (μ_B), and the magnetic moments of each of the elements in the X_2MnZ Heusler alloys. The X component is a $4d$ element and Pt, and Z = Al, Ga, In, Si, Ge, and Sn. The values in brackets are experimental data.

X_2MnZ	Mag. Mom. per unit cell(μ_B)	X(μ_B)	Mn(μ_B)	Z(μ_B)
Ru_2MnAl	2.15	-0.379	2.868	0.039
Ru_2MnGa	2.22	-0.433	3.092	-0.011
Ru_2MnIn	2.30	-0.526	3.328	0.021
Ru_2MnSi	3.05	-0.089	3.191	0.039
Ru_2MnGe	3.06	-0.134	3.316	0.013
Ru_2MnSn	3.11	-0.229	3.483	0.086
Rh_2MnAl	4.29	0.237	3.860	-0.037
Rh_2MnGa	4.32	0.222	3.960	-0.080
Rh_2MnIn	4.49	0.211	4.090	-0.015
Rh_2MnSi	4.59	0.335	3.907	0.017
Rh_2MnGe	4.65 (**4.30**)[**?**]	0.348	3.995	-0.038
Rh_2MnSn	4.74	0.310	4.075	0.039
Pd_2MnAl	4.24(**4.40**)[**?**]	0.059	4.150	-0.023
Pd_2MnGa	4.30	0.084	4.242	-0.109
Pd_2MnIn	4.33(**4.30**)[**?**]	0.043	4.303	-0.053
Pd_2MnSi	4.18	0.054	4.096	-0.024
Pd_2MnGe	4.21(**3.2**)[**?**]	0.076	4.181	-0.115
Pd_2MnSn	4.32(**4.23**)[**?**]	0.032	4.246	0.008
Pt_2MnAl	4.21	0.090	4.051	-0.018
Pt_2MnGa	4.25	0.105	4.121	-0.084
Pt_2MnIn	4.35	0.087	4.220	-0.049
Pt_2MnSi	3.96	0.048	3.924	-0.063
Pt_2MnGe	4.15	0.086	4.065	-0.083
Pt_2MnSn	4.17	0.040	4.128	-0.042

In these systems the half-metallic properties have not been reported experimentally. Our results indicate that a candidate may be Ru_2MnGe with a negligible ratio. Other two systems with a small value (0.02) are Ru_2MnSi and Ru_2MnSn.

In Table **??**, we show the results for the magnetic moment per unit cell and the contributions coming from the three chemical elements. In the cases where experimental values are reported, we show them in brackets and bold face. In the Ru series, this element couples

TABLE VI. Structural properties of the X_2MnZ Heusler alloys. X is an element of the 4*d* series, and Pt, and Z = Al, Ga, In, Si, Ge, and Sn. The crystalline structure are cubic or tetragonal, when both structures are close in energy their characteristics are given. The lattice constant is given in (Å), and the binding energy in eV/atom. The values in brackets are experimental data.

X_2MnZ	Lattice Parameter ($\AA$)	Binding Energy (eV/atom)
Ru_2MnAl	6.054	-5.475
Ru_2MnGa	6.138	-5.052
Ru_2MnIn	6.281	-4.751
Ru_2MnSi	5.958	-5.842
Ru_2MnGe	6.066	-5.516
Ru_2MnSn	6.284	-5.143
Rh_2MnAl	6.120	-5.298
Rh_2MnGa	6.210	-4.897
Rh_2MnIn	6.352	-4.660
Rh_2MnSi	6.023	-5.470
Rh_2MnGe	6.138 (**5.998**)[**?**]	-5.207
Rh_2MnSn	6.350	-4.965
Pd_2MnAl	2×6.343, 6.088	-4.182
	6.246(**6.165**)[**?**]	-4.180
Pd_2MnGa	2×6.430, 6.138	-3.856
	6.330	-3.854
Pd_2MnIn	2×6.612, 6.268	-3.635
	6.486(**6.373**)[**?**]	-3.633
Pd_2MnSi	2×6.194, 6.129	-4.202
	6.162	-4.201
Pd_2MnGe	6.282 (**6.134**) [**?**]	-4.050
Pd_2MnSn	6.486(**6.380**)[**?**]	-3.864
Pt_2MnAl	2×6.505, 5.817 (**6.24**)[**?**]	-5.286
Pt_2MnGa	2×6.594, 5.872 (**6.16**)[**?**]	-4.865
Pt_2MnIn	2×6.820, 5.923	-4.649
Pt_2MnSi	2×6.561, 5.552	-5.208
Pt_2MnGe	2×6.690, 5.665	-5.004
Pt_2MnSn	2×6.887, 5.806	-4.834

antiferromagnetically to Mn, but the Z elements couple ferromagnetically to give rise to magnetic moments per unit cell that goes from 2.15 to 3.11 μ_B. In the Rh, Pd, and Pt series the X elements and Mn contribute positively to produce magnetic moments per unit cell in the range 3.96 (Pt_2MnSi) to 4.74 (Rh_2MnSn) μ_B.

It is important to recall that these results are obtained with an atomic base of 16 atoms, and all are ferromagnetic. In the reported literature, the Mn magnetic moment in Rh_2MnGe, Pd_2MnGe, Pd_2MnGe, and Pd_2MnSn, couple ferromagnetically but in Pd_2MnAl, Pd_2MnIn, Pt_2MnAl, and Pt_2MnGa they couple antiferromagnetically. The later systems must be studied with a large enough atomic unit to be able to describe the three different types of antiferromagnetism characteristic of Heusler Alloys. In the ferromagnetic cases the agreement between theory and experiment are very good, except for the case of Pd_2MnGe, in which the calculated magnetic moment is 4.21 μ_B and the one measured[**?**] is 3.2 μ_B

In Table **??** we give the results for the lattice parameter in Åand the cohesive energy in eV. The Ru, Rh and Pt series are cubic. In the Pd series, four cases are tetragonal (Z=Al, Ga, In, and Si). In the Table we give the dimensions of the base and hight of the cell. The cases that we can compare are those that are ferromagnetic (Rh_2MnGe, Pd_2MnGe, and Pd_2MnSn). The comparison with the experimental values are good. In the antiferromagnetic cases, we give the values of the ferromagnetic phase and include the measured values.

X_2MnZ with X = Cu, Ag, Au, and Z = Al, Ga, In, Si, Ga, and Sn

The cases in which the X element is a noble metal, X= Cu, Ag and Au are discussed now. In Fig. 7 we present the total SPLDS and the individual SPLDS for the case Cu_2MnAl. In the upper figure, we see that the Cu d sub-bands are completely filled (blue curve). In contrast, as seen in the middle figure, the spin-down Mn sub-band is mostly empty, and as we will discuss bellow, gives rise to the magnetic properties of the alloy (see black curve in the upper panel). The Al densities of states are presented in the lower panel. Here, again the electron occupancy in spin-up and spin-down are also very similar and do not contribute significantly to the total magnetic moment. The $3s$ and $3p$ electrons just contribute to the electron conductivity.

In Figure 8, the total spin polarised densities of states for up- and down-spin of the six Cu-alloys are shown. The general behavior for the six alloys is very similar to the Al-case. In

TABLE VII. Transferred electronic charges between the atoms of the X_2MnZ Heusler like systems with X = Cu, Ag, Au, and Z= Al, Ga, In Si, Ge and Sn. In the last column we give the ratio between the electronic densities of states of opposite spins (the larger over the smaller).

X_2MnZ	X(Charge) (e)	Mn(Charge) (e)	Z(Charge) (e)	DOS ratio
Cu_2MnAl	0.297	-1.031	0.437	0.42
Cu_2MnGa	0.217	-1.001	0.568	0.23
Cu_2MnIn	0.730	-1.216	-0.245	0.45
Cu_2MnSi	0.468	-1.029	0.095	0.62
Cu_2MnGe	0.132	-1.068	0.804	0.01
Cu_2MnSn	0.764	-1.015	-0.514	0.04
Ag_2MnAl	0.278	-1.042	0.486	0.93
Ag_2MnGa	0.295	-1.142	0.553	0.85
Ag_2MnIn	0.617	-1.235	0.000	0.33
Ag_2MnSi	0.367	-1.105	0.372	0.50
Ag_2MnGe	0.177	-1.063	0.709	0.22
Ag_2MnSn	0.585	-1.013	-0.157	0.53
Au_2MnAl	-0.0885	-0.949	1.126	0.67
Au_2MnGa	-0.1237	-1.026	1.272	0.20
Au_2MnIn	0.032	-1.092	1.029	0.22
Au_2MnSi	0.011	-1.041	1.018	0.45
Au_2MnGe	-0.103	-0.999	1.206	0.93
Au_2MnSn	0.284	-1.019	0.452	0.21

the systems with Z belonging to the IIIA column (Al, Ga, and In) a week hybridization with the Cu states, in the deep energy values, is observed, whereas in the IVA column elements of the periodic table, the s-band are so deep in energy that do not hybridize much with the rest of the electrons.

In Table **??**, we present the results for the electron distribution in the three atomic components of the noble metal series. In the second to fourth columns, we give the difference between the total number of electron of each element in the atomic case minus that number when they are alloyed. As in previous cases, Mn transfers about one electron to the other components. In the Cu series there is a modest charge transfer to Cu, except for the In and Sn alloys. In those two alloys, In and Sn transfer also electrons to the Cu atoms. In

TABLE VIII. Magnetic moment per unit cell (μ_B), and the magnetic moments of each of the elements in the X_2MnZ Heusler alloys. The X element is a noble metal, and Z = Al, Ga, In, Si, Ge, and Sn. The values in brackets are experimental data.

X_2MnZ	Mag. Mom. per unit cell (μ_B)	X(μ_B)	Mn(μ_B)	Z(μ_B)
Cu_2MnAl	3.64(**3.80**)[**?**]	-0.031	3.803	-0.103
Cu_2MnGa	3.70	-0.020	3.933	-0.200
Cu_2MnIn	3.79(**4.00**)[**?**]	-0.080	4.050	-0.094
Cu_2MnSi	3.96	-0.020	3.899	0.095
Cu_2MnGe	4.14	0.046	4.058	-0.010
Cu_2MnSn	4.12 (**4.11**)[**?**]	-0.032	4.097	0.088
Ag_2MnAl	3.82	-0.058	4.084	-0.148
Ag_2MnGa	4.19	0.011	4.302	-0.129
Ag_2MnIn	4.22	-0.021	4.393	-0.132
Ag_2MnSi	4.26	-0.009	4.259	0.014
Ag_2MnGe	4.26	0.033	4.271	-0.081
Ag_2MnSn	4.24	-0.056	4.332	0.024
Au_2MnAl	3.82	-0.013	4.043	-0.200
Au_2MnGa	4.05	0.029	4.210	-0.222
Au_2MnIn	4.09	0.004	4.324	-0.237
Au_2MnSi	4.14	0.024	4.206	-0.113
Au_2MnGe	4.23	0.051	4.253	-0.126
Au_2MnSn	4.22	-0.016	4.349	-0.102

the rest of the Cu systems the Z component also receive charge. In the Ag alloys, we have a similar behavior, except in Ag_2MnSn, in which Sn donates 0.16 electrons. In the case of the Au systems, most of the charge transfer goes to the Z element, Al, Ga, In, Si, and Ge receive more than 1 electron and Sn 0.452 electrons. Au donates in the cases of Z= Al, Ga, and Ge and receives electrons for Z=In, Si, and Sn. In the last column we observe that the ratio between the value for the total spin polarized electronic densities of states, spin-up and spin-down is small (0.01) only in the case of Cu_2MnGe.

The magnetic moments per unit cell and in each one of the components are presented in Table **??**. There are experimental data available only for the Cu systems with Z=Al, In, and Sn. The values are given in brackets and bold face. The difference between the calculated

TABLE IX. Structural properties of the X_2MnZ Heusler alloys. The X element is a noble metal, and Z = Al, Ga, In, Si, Ge, and Sn. The crystalline structure are cubic or tetragonal, when both structures are close in energy their characteristics are given. The lattice constant is given in (Å), and the binding energy in eV/atom. The values in brackets are experimental data.

X_2MnZ	Lattice Parameter ($\AA$)	Binding Energy (eV/Atom)
Cu_2MnAl	6.042(**5.950**) [**?**]	-3.527
Cu_2MnGa	6.126	-3.224
Cu_2MnIn	6.318(**6.200**) [**?**]	-2.990
Cu_2MnSi	5.993	-3.574
Cu_2MnGe	6.114	-3.437
Cu_2MnSn	6.342(**6.170**) [**?**]	-3.189
Ag_2MnAl	6.462	-2.898
Ag_2MnGa	6.570	-2.657
Ag_2MnIn	6.746	-2.501
Ag_2MnSi	6.478	-2.875
Ag_2MnGe	6.571	-2.826
Ag_2MnSn	6.798	-2.672
Au_2MnAl	6.462	-3.371
	2×6.482, 6.453	-3.369
Au_2MnGa	6.560	-3.059
	2×6.743, 6.266	-3.054
Au_2MnIn	6.726	-2.888
Au_2MnSi	2×6.691,6.155	-3.253
	6.498	-3.250
Au_2MnGe	6.594	-3.211
	2×6.781, 6.269	-3.208
Au_2MnSn	6.831	-3.026
	2×7.010, 6.448	-3.024

and measured values is 4.4 and 5.5 percent smaller for Z=Al and In, respectively and 0.2 percent larger for Z=Sn. One observes also that the major contribution to the magnetic moment comes from the Mn atoms and is around $4\mu_B$: Furthermore, the coupling between Mn and the other atoms is antiferromagnetic for most of the cases.

Finally, in Table **??** we present the results for the crystalline structure, lattice parameters, and the cohesive energy. The ground state crystalline structure in all the systems is cubic,

but in the Au series, the tetragonal structures are very close in energy. One can observe that the lattice parameter, given in the second column, the measured values in Au systems (Z=Al, In, and Sn), are in very fair agreement with our calculation.

CONCLUSIONS

Here, we presented a systematic study of the X_2MnZ Heusler alloys with X being a $3d$, $4d$, Pt, and noble metals Cu, Ag, and Au. The Y elements studied were the IIIA (Al, Si, and Ga) and IVA (Ge, In, and Sn) column elements. The spin polarized local electronic densities of states were calculated and the energy minimized as a function of electron occupation in the spin-up and spin-down sub-bands and cell geometry and size. The calculations were performed within the density functional theory using the SIESTA code. In general, one observes an important charge transfer from the Mn atoms to the other components. The half metallic behavior was observed in the Fe_2MnSi, Co_2MnSi, and Ru_2MnGe alloys. A less pronounced gap in the spin down density of states is obtained in Co_2MnGe, Ru_2MnSi, Ru_2MnSn, Cu_2MnGe, and Cu_2MnSn. The highest magnetic moment per unit cell (7.86 μ_B) is obtained in the Fe_2MnIn and the smallest (2.15μ_B) in Ru_2MnAl. With a unit of 16 atoms we obtain, for all the systems, as the ground state the phase in which all the Mn atoms couple ferromagnetically. However,it has been observed that in Pd_2MnAl, Pd_2MnIn, Pt_2MnAl, and Pt_2MnGa, they couple antiferromagnetically giving rise to complex antiferromagnetic phases. A theoretical study with a larger atomic cell is necessary to explore those phases. The crystalline structure and the lattice parameter agree well with the experimentally reported systems.

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Figure.1 The X_2MnZ unit cell used in the electronic structure calculation. The Mn atoms are denoted by light brown circles, the X elements (Co, Fe, Ni, Cu, Ru, Rh, Pd, Ag, Pt, Au) by pink circles and the Z atom (Al, Si, Ga, Ge, In, and Sn) by blue circles.

Figure 2, Positions that occupy the chemical elements X, Mn, and Z, in the Periodic Table, constituting the Heusler alloys studied here. The X are highlighted in yellow and Z elements in green and brown. Figure 3. Electronic spin polarized local density of states (SPLDS) for the Co_2MnAl alloy. In the upper panel we show the total spin polarized densities of states (black line) and the $3d$ Cobalt contribution (purple line). In the central panel we present the electronic structures at the Mn atoms; the $3d$ (in blue), and the $4s$ (in red). In the bottom panel, we show the Al electronic structure; the $3p$ (in green) and the $3s$ (in light brown). Notice that the lower panel has a different vertical scale.

Figure 4. Total electronic spin polarized local density of states for the six Co systems Z=Al, Si, Ga, Ge, In, and Sn.

Figure 5. Electronic spin polarized local density of states (SPLDS) for the Pd_2MnAl alloy. In the upper panel we show the total spin polarized densities of states (black line) and the $3d$ Palladium contribution (purple line). In the central panel we present the electronic structures at the Mn atoms; the $3d$ (in blue), and the $4s$ (in red). In the bottom panel, we show the Al electronic structure; the $3p$ (in green) and the $3s$ (in light brown). Notice that the lower panel has a different vertical scale.

Figure 6. Total electronic spin polarized local density of states for the six Pd systems Z=Al, Si, Ga, Ge, In, and Sn.

Figure 7, Electronic spin polarized local density of states (SPLDS) for the Cu_2MnAl alloy. In the upper panel we show the total spin polarized densities of states (black line) and the $3d$ Copper contribution (purple line). In the central panel we present the electronic structures at the Mn atoms; the $3d$ (in blue), and the $4s$ (in red). In the bottom panel, we show the Al electronic structure; the $3p$ (in green) and the $3s$ (in light brown). Notice that the lower panel has a different vertical scale.

Figure 8. Total electronic spin polarized total local density of states for the six Cu systems Z=Al, Si, Ga, Ge, In, and Sn.