Minority-spin polarization and surface magnetic enhancement in Heusler clusters

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Real space pseudopotential calculations are used in order to investigate the properties of Co-based Heusler clusters. Co-Mn-Ga clusters are examined with respect to their stability, structure, and electronic spin polarization. The half metallic behavior, observed in bulk materials, does not apply in the case of clusters owing to a surface contribution: we find a strong enhancement of the magnetism in these clusters. In particular, we observe a large minority spin polarization, which can be important for nanoengineering of magnetoresistance devices.

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In 1903, German chemist and engineer Fritz Heusler synthesized ternary metallic alloys with rather unusual magnetic properties: They are ferromagnetic, although the constituent elements may not be ferromagnetic.[1] These materials are known as "Heusler alloys." Their chemical formula is X_2YZ, where X=Fe, Co, Ni, Cu, Pd, Pt, etc., usually Y=Mn, and Z=Al, Si, Ga, Ge, In, Sn, Sb, etc. The crystal structure at room temperature is usually cubic, $L2_1$ (Fig. 1), and can be considered as four interpenetrating *fcc* sublattices with atoms in the positions, $X_1(000)$, $Y(\frac{1}{4}\frac{1}{4}\frac{1}{4})$, $X_2(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, and $Z(\frac{3}{4}\frac{3}{4}\frac{3}{4})$.[2]

Some Heusler alloys (such as Co_2MnGa) have been predicted theoretically to be half metallic.[4,5] This property implies that the majority spin electrons are metallic while the minority spin electrons are semiconducting. Figure 2 illustrates the spin polarization of the electronic density of states at the Fermi energy. Considerable work has been made to achieve the theoretically predicted 100% spin polarization in the experimental studies.[6,7] However, experimental studies have shown that defects of any kind, especially interfaces, tend to fill the energy gap for the minority spin states. Consequently, the spin polarization is considerably reduced and may even vanish.[8] An approach to achieve the desired polarization combines efforts in fabricating as perfect crystals and interfaces as possible.[9]

Although most of the bulk properties of the Heusler alloys have been found to be interesting for applications, there have been attempts of reducing their dimensionality. The Heusler alloys have been successfully grown epitaxially.[10–14] Their lattice parameters are compatible with some semiconductors such as GaAs, promising a good integration into the existing semiconductor technology.[9,15] Pulse laser deposition has also been successfully used for growing thin films of Heusler alloys.[16,17] In case of nonstoichiometric NiMnGa thin films, a tendency was observed to segregate with an appearance of stoichiometric Ni_2MnGa nanophase.[18] Crystallites of Ni_2MnGa with 20–50 nm size emerged, surrounded by quasiamorphous matrix.

One can imagine that the Heusler clusters can be considered to be promising for nanotechnology. Heusler alloys at a reduced dimensionality may result in technologically relevant changes of the material properties. Unfortunately, there are hardly any studies for the Heusler alloys, which is in contrast to the studies of semiconducting and pure-metallic nanocrystals, which have been extensively developed.[19–21] Based on our previous experience in the physics of clusters, we aim to explore the possible advantages of using the Heusler alloys in the nanotechnologies. Here, we focus on the Co_2MnGa clusters and address the issues of their stability and magnetic properties.

For the electronic structure calculations, we employ norm-conserving pseudopotentials constructed within the framework of the local spin density approximation (LDA) of the density functional theory.[22–24] The Kohn–Sham equations are solved on a real space grid using the high-order finite difference method implemented in the code PARSEC.[25] A grid spacing of 0.2 a.u. (1 a.u.=0.529 Å) has been used. The fine grid spacing is in contrast to the semiconductor elements where a spacing of more than twice this size can be employed. A separation of at least 8 a.u. between the outermost atoms and the spherical boundary were used throughout. The local-density functional of Ceperley and Alder was used as parametrized by Perdew and Zunger.[26,27] The PARSEC code solves the Kohn–Sham equation by a series of subspace filtering iterations with Chebyshev polynomials, which reduces the overall numerical effort by as much as an order of magnitude when compared to performing an exact diagonalization.[28] We make use of the symmetry and paral-

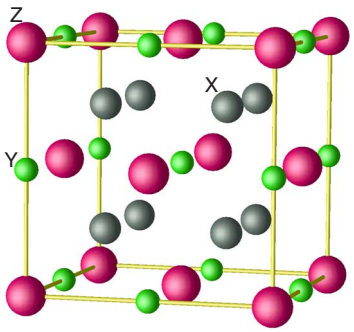

FIG. 1. (Color online) The cubic $L2_1$ structure of the Heusler intermetallic phase. In this work, according to the chemical formula X_2YZ, X is Co, Y is Mn, and Z is Ga.

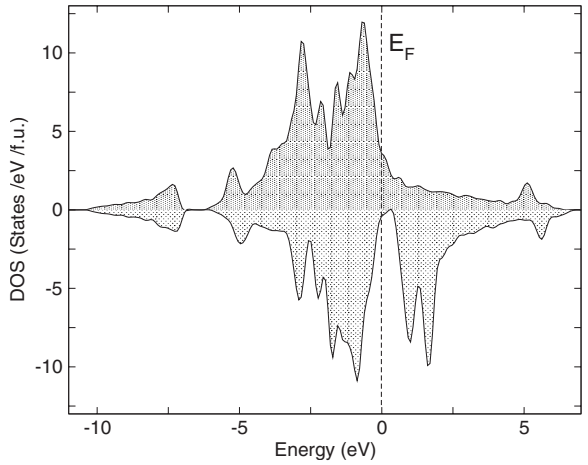

FIG. 2. The density of states for bulk Co_2MnGa. The gap in the minority spin channel determines the half-metallic behavior of this system. In case of Co_2MnGa, the minority spin gap given by standard density functional (using LDA or generalized gradient approximation) methods is not complete. A detailed analysis is given in Ref. 3.

lelization in PARSEC. The structure of the clusters are optimized with the final forces smaller than ~0.001 Ry/a.u. The binding energies of the clusters are calculated by subtracting the sum of the elemental energies of isolated atoms from the total energies of the relaxed clusters.

The lowest energy structure of Co_2MnGa is $L2_1$. It is cubic and, unlike Ni-based Heusler alloys, Co_2MnGa does not transform into other structures with lower symmetry.[29] For this study, we choose "bulklike" structures for the clusters with a Ga atom in the center. In order to construct these clusters, we built a large supercell of the $L2_1$ structure of Co_2MnGa and cut out spherical fragments with a specific radius. The two clusters that we selected to study are listed in Table I. Their chemical compositions are not perfectly stoichiometric. We chose these two particular clusters (65 and 169 atoms) because they are the most stoichiometric from all the range that we looked at, starting from 15 atoms and going up to 169 atoms. Note that the clusters are metallic and no passivation of the surface is made in contrast to the quantum dots of semiconductor materials.[30]

The clusters have been relaxed but no diffusion was allowed. The atomic order remains as it was initially made and in accordance with the perfect Heusler structure. Surface relaxation is noticeable and appears to affect bonding in the two atomic layers that are close to the surface (see Fig. 3). In this sense, the smaller cluster has very little of the original

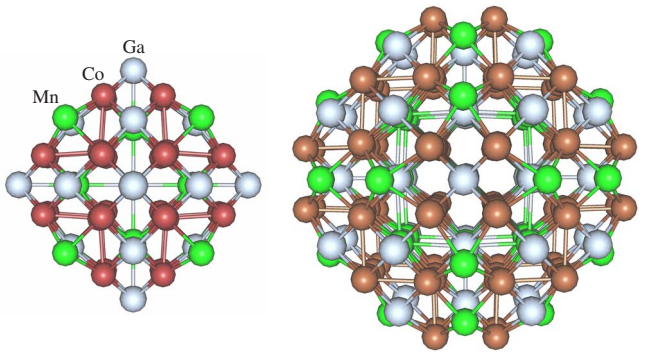

FIG. 3. (Color online) The two clusters that are studied in this work. Relaxation showed that the two outer layers of the clusters experience noticeable relaxations while the inner structure is bulklike. From this point of view, the properties of the 65-atoms cluster are mostly determined by the surface. The 169-atoms cluster is large enough to exhibit both surface and bulk properties.

Heusler bulk nature. The 169-atoms cluster, on the other hand, might exhibit bulklike behavior since its core is not distorted. The estimated binding energies of the two clusters are listed in Table I.

We find the clusters to be ferromagnetic. Their magnetic moments are listed in Table I and are higher than the bulk value. Partial magnetic moments are significantly higher as compared to the bulk values (see Table II). Figure 4 shows mapping of the spin density in three different planes of the 169-atoms cluster. The magnetic moments of Co atoms are smaller than on Mn although the number of Co atoms is double of the Mn; therefore, the contributions of Co and Mn are comparable. The enhancement of the magnetism is mostly a surface effect. Within the cores of the clusters, the atoms have smaller spin polarization that are closer to the bulk values while the surface spin density is increased. This is consistent with the picture of the *p-d* hybridization in the Heusler alloys discussed by Kübler *et al.* in Ref. 31. The *p-d* hybridization reduces the magnetic moments. On the surface layers, the degree of *p-d* hybridization is smaller than in the bulk whereby the surface magnetic moments become larger. Similar conclusions were made by Lee *et al.* who studied the surface magnetization in Co_2MnSn.[33]

The electronic spin density distributions shown in Fig. 5 reveal important changes of the electronic properties. While the bulk system is majority spin polarized, the clusters demonstrate an opposite picture where the minority spin states have a much larger population at the Fermi level. The gap that existed in the bulk material is completely filled by the surface states. The majority spin states have been shifted to

TABLE I. The number of atoms, atomic compositions, normalized atomic compositions, energy of formation, and magnetic moments of the clusters studied in this work. The clusters are chosen to be Ga-centered and have bulklike structures before the relaxation.

Number of atoms	Atomic composition	Per formula unit	E_B (eV/*at*)	$\mu(\mu_B/at)$
65	$Co_{32}Mn_{14}Ga_{19}$	$Co_{2.13}Mn_{1.6}Ga_{0.27}$	−3.4322	1.69
169	$Co_{88}Mn_{38}Ga_{43}$	$Co_{1.88}Mn_{1.88}Ga_{0.24}$	−3.765	1.76
Bulk	-	Co_2MnGa	-	1.02

TABLE II. Calculated partial magnetic moments in the larger cluster with 169 atoms. Cutoff radii for subtraction the two spin components of the spin density are 2.32, 2.18, and 2.50 a.u. for Mn, Co and Ga, respectively.

	Mn	Co	Ga
Surface	4.93	2.16	−0.16
Intermediate	4.26	1.71	−0.12
Center	-	1.24	−0.03
Bulk[a]	2.78	0.73	-

[a]See Ref. 3.

the lower energies by about 2 eV as compared to the bulk case (compare with Fig. 2). From the DOS population at the Fermi level, we can estimate the spin polarization, P, by using the formula $P=(N_{\uparrow}-N_{\downarrow})/(N_{\uparrow}+N_{\downarrow})$. (For more rigorous calculations of the spin polarization, see Ref. 32). We find ~80% minority spin polarization of the conductance electrons. However, this property will be present as long as the clusters have a free standing surface. This brings us to the idea that the surface physics of Heusler systems has to be addressed in the future studies.

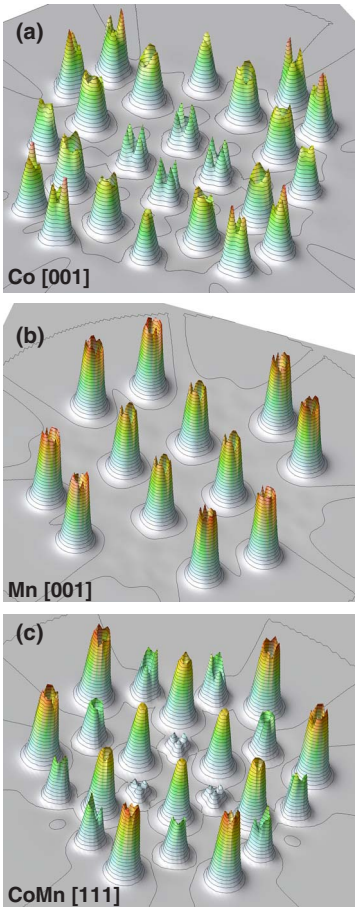

FIG. 4. (Color online) The spin density of the 169-atoms cluster shown in three different planes: (a) Co [001], (b) Mn [001], and (c) CoMn [111] planes. Co and Mn atoms gain higher spin polarization as it gets closer to the surface of the cluster.

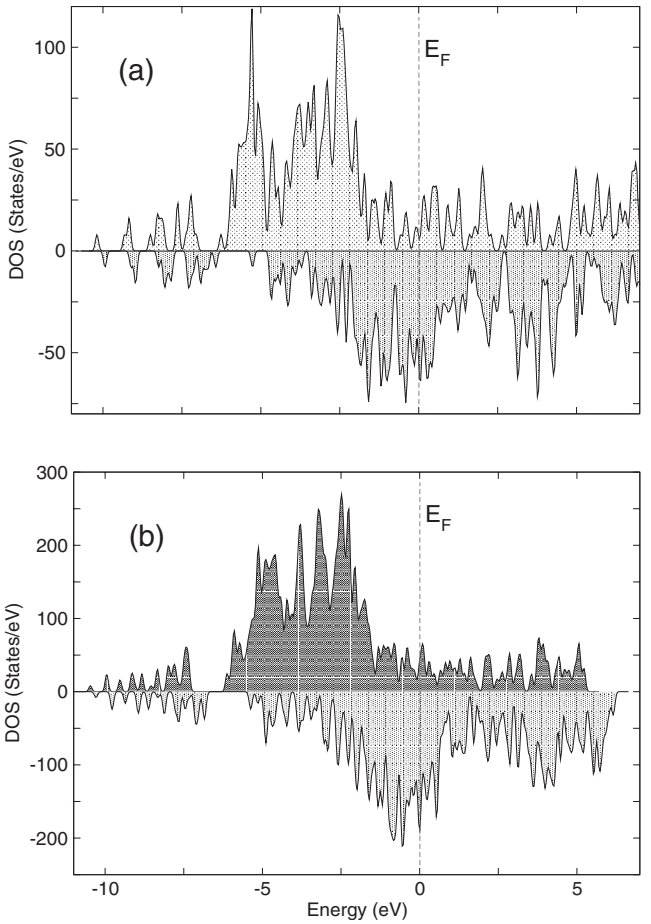

FIG. 5. Total densities of states: (a) The 65-atoms $Co_{32}Mn_{14}Ga_{19}$ and (b) the 169-atoms $Co_{88}Mn_{38}Ga_{43}$ clusters. Both clusters demonstrate a negative, about 80%, electronic spin polarization at the Fermi energy.

In summary, we used a real space pseudopotential method to investigate the properties of the Heusler clusters Co-Mn-Ga. Two clusters, with stoichiometry close to Co_2MnGa, were selected and examined with respect to their structural and magnetic properties. We find that unlike the bulk, Co-Mn-Ga clusters cannot be characterized as majority spin-polarized half metals. The bulk gap in the minority states is filled by the surface states. As a consequence, the clusters in this case possess a minority spin polarization of the order of 80%. This could be a valuable property for applications where the magnetoresistance is employed. It may be that the Heusler clusters offer a new and, heretofore, unexplored type of materials.

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