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Effect of disorder on the magnetic properties of cubic Mn_2Ru_xGa compounds: A first-principles study

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We perform first-principles electronic structure calculations to explain the anomalous magnetic behavior of the Mn_2Ru_xGa compounds upon Ru doping as shown experimentally recently by Kurt *et al.* [Phys. Rev. Lett. **112**, 027201 (2014)]. Our results suggest that disorder caused by the distribution of the Mn and Ru atoms at various sites reproduces the experimental data. All compounds present antiparallel alignment of the neighboring Mn magnetic moments and, with the exception of Mn_2RuGa, none of them presents half metallic behavior. © *2014 AIP Publishing LLC*.
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I. INTRODUCTION

The developments in nanoelectronics, combining the magnetic and semiconducting materials (known as spintronics)[1,2] have brought the half-metallic magnets to the center of scientific research.[3] In these materials, the two spin bands show a completely different behavior. While the spin-up electronic band structure is metallic, in the spin-down band the Fermi level falls within an energy gap as in semiconductors.[3] Such half-metallic compounds exhibit, ideally, a 100% spin polarization at the Fermi level and therefore they should have a fully spin-polarized current and be ideal spin injectors into a semiconductor, thus maximizing the efficiency of spintronic devices.[4]

Heusler compounds are a promising family to achieve half-metallicity since they encompass a large number of members, they crystallize mostly in cubic structures similar to the zincblende structure of semiconductors and several have very high Curie temperatures.[5] Several among them have been predicted to be half-metals and in case of half-metallicity the total spin magnetic moment in the unit cell is intrinsically connected to the total number of valence electrons.[6–8] This behavior is usually referred to as "Slater-Pauling rules" in literature (see Refs. 6–8 for an extended discussion). The search for Heusler compounds presenting half-metallic behavior led to a large number of both experimental and theoretical studies.[5] In this respect in Ref. 9, Kurt and collaborators reported an extensive study on the magnetic properties of Mn_2Ru_xGa thin films as a function of the Ru concentration. They have shown that the total spin magnetic moment shows a change in its behavior around $x = 0.5$ which authors attributed to the existence of a half-metallic fully compensated ferrimagnetic state for $Mn_2Ru_{0.5}Ga$. Authors also claimed that their results suggested that Mn_2Ru_xGa is a half-metal around $x = 0.5$ and increasing Ru concentration leads to a crossing of the minority-spin energy gap. Moreover, Kurt *et al.*, in Ref. 9, showed that all samples crystallize in an almost cubic structure, characteristic of Heusler compounds with a lattice constant of 5.97 Å and Extended X-Ray Absorption Fine Structure (EXAFS) measurements proved that there is no Ru-Ru or Ga-Ga nearest neighbors.

II. MOTIVATION AND COMPUTATIONAL DETAILS

Unfortunately, there is no direct experimental evidence in Ref. 9 for the half-metallicity of the Mn_2Ru_xGa compounds. This is crucial since if these compounds are actually half-metals, they could pave the way for spintronic devices with enhanced functionalities. To elucidate the origin of the magnetic behavior observed experimentally in Mn_2Ru_xGa compounds, we employ state-of-the-art first-principles electronic structure calculations. We use the full-potential nonorthogonal local-orbital minimum-basis band structure scheme (FPLO)[10] within the generalized gradient approximation (GGA),[11] and consider large supercells to simulate the fractional Ru concentration in the Mn_2Ru_xGa compounds. We were not able to determine the energetics since differences between total energies converge much slower with the number of **k**-points in the reciprocal space than total energies themselves and our computer resources were not sufficient. We should note that the ordered end compounds Mn_2Ga and Mn_2RuGa crystallize in the $C1_b$ and *XA* structures, respectively, as shown in Fig. 1, and we can move continuously between them by adding Ru atoms at the C site. For all calculations, we have used the experimentally determined lattice constant of 5.97 Å.[9] The very small tetragonalization of the lattice observed in the experiments only marginally affects our results and thus has been neglected.[12] Our results suggest that actually it is the disorder caused by the distribution of the Mn and Ru atoms at the various sites which is responsible for the observed behavior of the total spin magnetic moment in the samples and $Mn_2Ru_{0.5}Ga$ is not a half-metal contradicting the assumption in Ref. 9.

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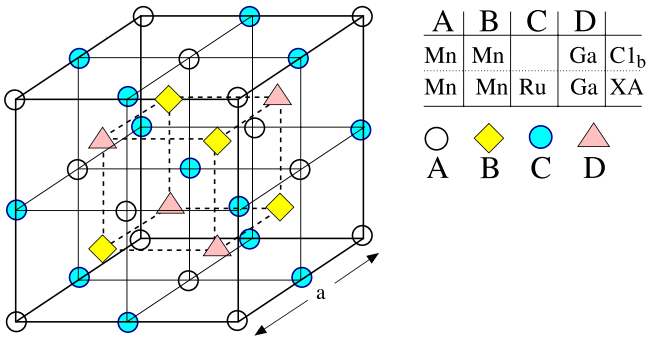

FIG. 1. Schematic representation of the $C1_b$ and *XA* structures of Heusler compounds. The lattice is an f.c.c. with four equidistant sites as basis along the diagonal. Note that the large cube contains exactly four primitive unit cells.

III. RESULTS AND DISCUSSION

A. Mn_2Ga

First, we consider the case of Mn_2Ga. As stated also in Ref. 9, if Mn_2Ga was a half-metal it would have a total spin magnetic moment of $-1\,\mu_B$.[6] Experiments gave a value of $-1.65\,\mu_B$ per formula unit (f.u.). Our calculations for Mn_2Ga in the perfect $C1_b$ structure gave an antiferromagnetic coupling of the Mn atoms at the A and B sites as expected from the Bethe-Slater curve and observed also in other cases of Mn-based Heusler compounds.[13] The two Mn atoms have absolute values of the spin magnetic moments exceeding the $3\,\mu_B$ which almost cancel each other (Ga carries a negligible spin moment as in other Heusler compounds)[8] and thus there is a very small total spin magnetic moment of $-0.02\,\mu_B$ per unit cell. In Table I, we have gathered the total spin magnetic moments for all studied cases expressed per formula unit. The density of states (DOS) presented in Fig. 2 reveals that there is actually a pretty large energy gap in the minority spin band structure just above the Fermi level and one could envisage that contraction of the lattice can shift the Fermi level higher in energy within the gap establishing a half-metallic behavior. Since, no information is provided in Ref. 9 on the exact position of the Mn atoms at the various sites, we consider a supercell containing 8 unit cells (two times the cube in Fig. 1) with 8 Mn atoms at the A site, 5 at the B site, and 3 at the C site. The Mn atoms at the A and C sites (which have the same local environment) have negative spin moments while the Mn atoms at the B sites have positive moments with values close to the perfect Mn_2Ga compound just discussed. Our calculation for the $[Mn_8]^A[Mn_5]^B[Mn_3]^C[Ga_8]^D$ supercell, where letters denote the various sites for clarity reasons, results in a total spin magnetic of $-12.4\,\mu_B$, which is reduced to $-1.55\,\mu_B$ when expressed per $Mn^A[Mn_{0.625}]^B[Mn_{0.375}]^CGa^D$ formula unit (see Table I). This value is very close to the experimental one of $-1.65\,\mu_B$. Moreover, as shown in Fig. 2, the disordered compound is not half-metallic any more. Note that we have performed calculations (not presented here) where Mn atoms from the A site, instead of the B site, migrate to the C site. But the obtained DOS and spin moments were similar to the perfectly ordered Mn_2Ga compound since A and C sites have the same local environment and the same symmetry.

TABLE I. Total spin magnetic moments in μ_B for all compounds under study expressed per formula unit. Superscripts denote the site occupied by the atoms. In all cases, signs of the total spin moments are such that the spin magnetic moments of the Mn atoms at A and C sites are negative.

Mn_2Ga	
Ideal half-metal	−1.00
$Mn^A\,Mn^B\,Ga^D$	−0.02
$Mn^A\,[Mn_{0.625}]^B\,[Mn_{0.375}]^C\,Ga^D$	−1.55
$Mn_2Ru_{0.5}Ga$	
$Mn^A\,Mn^B\,[Ru_{0.5}]^C\,Ga^D$	0.73
$Mn^A\,[Mn_{0.875}]^B\,[Mn_{0.125}Ru_{0.5}]^C\,Ga^D$	−0.05
Mn_2RuGa	
Ideal half-metal	1.00
$Mn^A\,Mn^B\,Ru^C\,Ga^D$	1.00
$[Mn_{0.75}Ru_{0.25}]^A\,Mn^B\,[Ru_{0.75}Mn_{0.25}]^C\,Ga^D$	1.01
$Mn^A\,[Mn_{0.75}Ru_{0.25}]^B\,[Ru_{0.75}Mn_{0.25}]^C\,Ga^D$	∼ −0.00

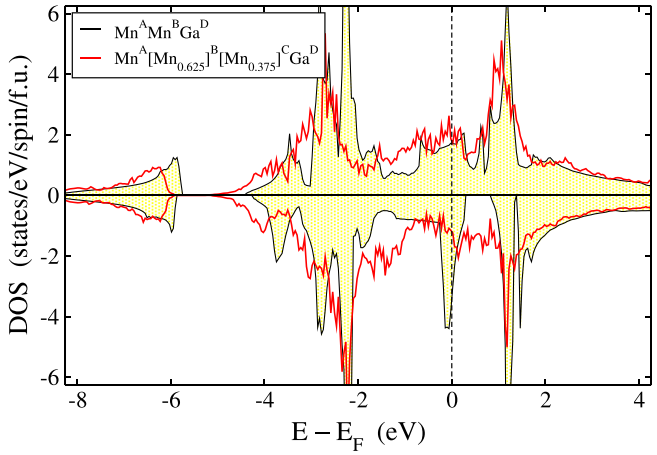

FIG. 2. Total DOS for the Mn_2Ga compound in the perfect $C1_b$ and the disordered cases. Zero energy denotes the Fermi level. DOS is drawn considering that the Mn atoms at the A and C sites have negative spin magnetic moments.

B. Mn_2RuGa

For the case of Mn_2RuGa, our calculations for the perfect *XA* structure gave a total spin moment of $1\,\mu_B$ and the DOS is that of a half-metal with an almost vanishing spin-down gap at the Fermi level (shaded line in Fig. 3). This agrees with the Slater-Pauling rule since Mn_2RuGa has in total 25 valence electrons per unit cell.[8] Experiments in Ref. 9 produced a value of about $0.5\,\mu_B$ half of our calculated value. We have performed calculations for a supercell containing 4 unit cells where swap takes place between Ru atoms and Mn atoms either at the A or B site keeping the stoichiometry. When we exchange Ru and Mn atoms at the A and C sites the total spin magnetic moment scarcely changes as shown in Table I, since A and C sites have the same local environment (each A or C site has four B and four D sites as nearest neighbors). The swap between Ru atoms and Mn atoms at B sites severely decreases the magnetization (see Table I) which almost vanishes when 25% of the Ru migrate to B site. In agreement with the behavior of the total spin magnetic moments in the case of Ru-Mn^A

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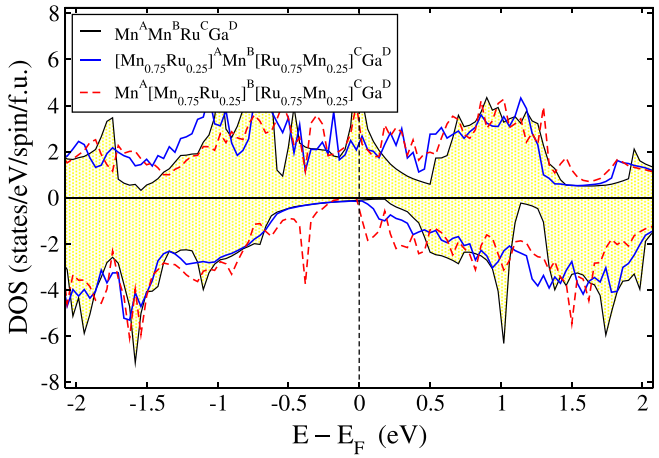

FIG. 3. Total DOS for the studied Mn_2RuGa compounds.

swaps, where Ru atoms occupy both A and C sites, (solid line in Fig. 3) the half-metallicity is preserved. On the contrary, in the case of Ru atoms at both B and C sites, the Fermi level falls within a peak in the minority-spin band structure and half-metallicity is lost.

C. $Mn_2Ru_{0.5}Ga$

One could envisage that a similar situation also holds for the $Mn_2Ru_{0.5}Ga$ case. For $Mn_2Ru_{0.5}Ga$, we perform, first, a calculation for a supercell containing 4 unit cells (the cube shown in Fig. 1) where Mn atoms occupy the ideal A and B sites, Ru the C sites, and Ga the D sites. For this supercell, we get a total spin magnetic moment of 2.9 μ_B and thus about 0.73 μ_B per $Mn_2Ru_{0.5}Ga$ formula unit. Mn atoms at the A site have spin moments of about $-3\,\mu_B$ and Mn atoms at the B sites slightly larger than 3.5 μ_B, while both Ru and Ga atoms carry moments one to two orders of magnitude smaller (Ru atoms about 0.2 μ_B and Ga atoms about 0.05 μ_B). Moreover, $Mn_2Ru_{0.5}Ga$ is not a half-metal as can be deduced from the DOS presented in Fig. 4. Second, we consider a supercell containing 8 unit cells where all eight A sites are occupied by Mn atoms, seven B sites are occupied by Mn atoms and one is vacant, and the remaining Mn atom occupies a C site. Our calculations for the $[Mn_8]^A[Mn_7]^B[MnRu_4]^C[Ga_8]^D$ compound yielded a total spin magnetic moment of $-0.38\,\mu_B$, which actually means less than $-0.05\,\mu_B$ per $Mn^A[Mn_{0.875}]^B[Mn_{0.125}Ru_{0.5}]^CGa^D$ formula unit. In this supercell, all Ru and Ga atoms occupy the ideal C and D sites, respectively, and thus the structure is coherent with the conclusions in Ref. 9 that there are no Ga-Ga or Ru-Ru nearest neighbors. The calculated total spin magnetic moment almost reproduces the experimental results. Moreover, the calculated DOS, presented in Fig. 4, shows no energy-gap and resembles the one for the perfect ordered case presented above. Note that we also carried out calculation (not presented here) where atomic swaps take place between Mn at the A sites and Ru atoms at the C sites, but A and C sites are equivalent with respect to their symmetry and results (spin magnetic moments and DOS) remained almost unchanged. A similar studied case where the compensation point at $x = 0.5$ is fortuitous and in reality it is induced by disorder is $Mn_{2-x}Co_xVAl$ studied in Ref. 14.

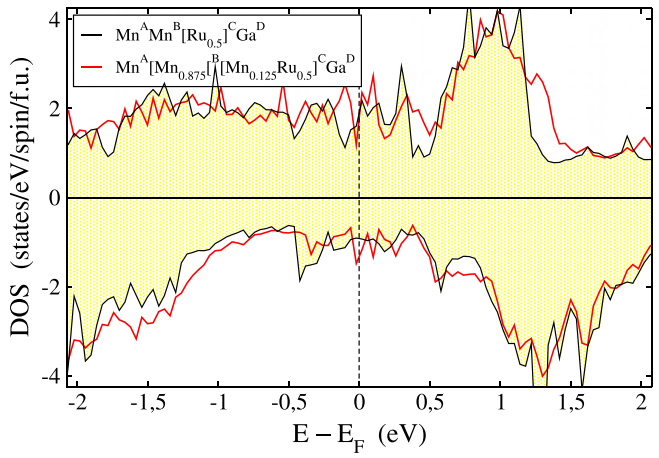

FIG. 4. Total DOS for the studied $Mn_2Ru_{0.5}Ga$ compounds.

D. Discussion

We now should briefly comment on the results and assumptions drawn in Ref. 9 based on the results of our first principles calculations. Our results suggest that the observed behavior of the magnetization versus the Ru concentration observed in experiments is more complex than assumed. The arguments in Ref. 9 were based mainly on the change of the number of valence electrons concentration as the Ru concentration increases. Our results suggest that at the same time a second procedure takes place involving the migration of Mn atoms to other sites. This plays a crucial role in the magnetic properties since Mn atoms at the B sites have antiparallel spin magnetic moments to the Mn atoms at the A and C sites and thus migration of the Mn atoms influences considerably the total spin magnetic moment.

To support the validity of our assumptions with respect to the interpretation of the experimental results, we have calculated the Curie temperature, T_c, within the mean field approximation taking into account all possible Mn-Mn interactions.[15] We found that T_c is 1530 K for the perfectly ordered Mn_2Ga compound in the $C1_b$ structure and 670 K for Mn_2RuGa in the perfectly ordered *XA* structure; these values are expected to be about 20% larger than the experimental values as for other half-metallic Heusler compounds.[15] However, Kurt *et al.* in Ref. 9 found a value of around 225 K, much smaller than the expected value, combined with a clearly nonzero magnetic moment of the compound. Our results suggest a severe structural disorder which is expected to lead to frustration of the exchange constants and thus to lower values of the T_c.

Point contact Andreev reflection (PCAR) spectroscopy measurements, employed in Ref. 9, are usually unsuitable to determine the intrinsic spin polarization of a material at the Fermi level since transport measurements scan not only the band structure of the sample but also the interface/surface properties, hot-spots, etc., which greatly influence the measured values. The value deduced by PCAR for $Mn_2Ru_{0.5}Ga$ of 54% is comparable to the one of a well-established nearly half-metallic compound such as Co_2MnSi of about 60%.[4] But several usual ferromagnets produce a similar result and

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thus PCAR is not a safe-method to search for half-metallic behavior.

Finally, we would also like to comment on the anomalous Hall effect (AHE) since it is used in Ref. 9 as a measure for crossing the spin gap because of its sign change. It is well known that several effects contribute to the AHE: the intrinsic contribution derived from the Berry curvature at the Fermi surface, the skew scattering, and the side jump scattering.[16] These can only be separated by their temperature dependencies and only the intrinsic contribution could have something to do with the spin gap. The other two contributions increase with increasing disorder and their sign can be positive or negative. The measured AHE is huge at $x = 0.33$, which may indicate serious disorder and possibly the sign change of the AHE indicates a disorder-order transition around $x = 0.5$ into the inverse Heusler type.

IV. SUMMARY AND CONCLUSIONS

We have performed first-principles calculations to explain the anomalous magnetic behavior presented by the Mn_2Ru_xGa compounds upon Ru doping as show experimentally recently.[9] Our study suggests that the observed magnetic behavior rises from disorder due to the distribution of the atoms (especially Mn atoms) at the various sites which deviate from the ideal $C1_b$ and *XA* lattice structures of perfect Heusler compounds. Moreover, the intermediate $Mn_2Ru_{0.5}Ga$ compounds are not half-metallic as assumed in Ref. 9. Our results provide a solid explanation for the results presented in Ref. 9 and could eventually lead to further experimental studies focusing on the role of disorder on the magnetic properties of Heusler compounds and its influence on half-metallicity.

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