Designing a fully-compensated half-metallic ferrimagnet

Mario Zic,1 Karsten Rode,2 Nagannivetha Thiagarajah,2 Yong-Chang Lau,2 Davide Betto,2 J.M.D. Coey,2 Stefano Sanvito,2 Kerry J. O’Shea,3 Ciaran A. Ferguson,3 Donald A. MacLaren,3 and Thomas Archer1,1

1 CRANN and School of Physics, Trinity College Dublin, Dublin 2, Ireland
2 CRANN, AMBER and School of Physics, Trinity College Dublin, Dublin 2, Ireland
3 SUPA, School of Physics & Astronomy, University of Glasgow, Glasgow G12 8QQ, United Kingdom

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Recent experimental work on Mn2Ru4Ga demonstrates its potential as a compensated ferrimagnetic half-metal (CFHM). Here we present a set of high-throughput ab initio density functional theory calculations and detailed experimental characterisation, that enable us to correctly describe the nominal Mn2Ru4Ga thin films, in particular with regard to site-disorder and defects. We then construct models that accurately capture all the key features of the Mn-Ru-Ga system, including magnetic compensation and the spin gap at the Fermi level. We find that electronic doping is necessary, which is achieved with a Mn/Ga ratio smaller than two. Our study shows how composition and substrate-induced biaxial strain can be combined to design the first room-temperature CFHM.

Compensated ferrimagnetic half metals (CFHM) have an ordered spin-state which results in half-metallicity, without any net magnetic moment. As the material creates no stray magnetic field it should have low Gilbert damping, and offer numerous advantages compared to standard ferromagnetic metals. These include higher frequency operation, higher packing density, reduced device power requirement and devices that are impervious to external magnetic fields. Although there is no net magnetic moment, the highly-polarised spin-state allows switching of the magnetisation via spin-transfer torque. The class of CFHMs was first envisaged by van Leuken and de Groot in 1995, but despite significant efforts the goal of a CFHM had proved elusive.

Recent experimental and theoretical efforts towards creating a CFHM have concentrated on the Heusler alloy system Mn2Ru4Ga (MRG). Heusler alloys are made of four interlaced fcc lattices, which form a bcc-like structure. Mn2RuGa has the full Heusler (L21) structure, with Mn occupying the 4a and 4c sites, Ru the 4d and Ga the 4b sites. Half-metallic Heuslers with the L21 structure are expected to follow a modified Slater-Pauling curve with the net magnetic moment m given by m = Nv − 24 where Nv is the number of valence electrons. For Mn2RuGa, Nv = 25, resulting in a net moment of 1μB. Mn2Ga was expected to have a half-Heusler (C15) structure, with Mn on 4a, 4c sites and Ga on 4b sites, thus leaving the 4d site empty. In half-metallic Heuslers with the C15 structure, the magnetic moment m is given by m = Nv − 18. For Mn2Ga, Nv = 17 and hence m = −1μB. The idea behind the Mn2Ru4Ga system, as proposed by Kurt et al., was that by changing the Ru content x a material can be formed mid-way between Mn2RuGa and Mn2Ga, that is half-metallic, yet presents no net magnetic moment.

Cubic Mn2Ru4Ga was stabilized in thin film form by Kurt et al., who showed that at x ≈ 0.5 there is an ordered spin state with a critical temperature of approximately 550 K and a very small net magnetic moment. In the same work Andreev reflection (PCAR) spectroscopy showed a 54% spin polarization at the Fermi level. This is less than the 100 % expected for an ideal half metal, but close to the values measured in other Heusler half-metals in thin film form. Further evidence of half-metallicity comes from the spontaneous Hall angle, more than an order of magnitude higher than that observed in the 3d-transition metals. This and the linear variation of m with x provided strong indications that Mn2Ru0.5Ga, grown by Kurt et al., was a CFHM.

However, despite the experimental evidence, the measurements do not match the theoretical understanding of Mn2Ru4Ga provided by Galanakis et al. There are three main areas where disagreement between theory and experiment exists, namely 1) the on-set of half-metallicity; 2) the cell volume; and 3) the dependence of M on x.

Half-metallicity

Density functional theory (DFT) investigations of Mn2Ru0.5Ga indicate that, although it may be possible to engineer a phase with zero magnetic
moment, this will not be half-metallic. Our calculations and those of others find that the spin gap in the density of states (DOS) of Mn$_2$Ru$_{0.5}$Ga lies about 0.4 eV above the Fermi level, $E_F$. In Fig. 1 we plot the calculated DOS and the corresponding resistivity, obtained by solving the Boltzmann equations in the relaxation time approximation. Although the DOS exhibits a large spin polarisation, $\approx 60\%$, this is not reflected in that of the resistivity, which is only 30\%. Since our transport calculations are expected to overestimate the spin polarization, the presence of the 'pseudo-gap' cannot justify the large experimentally observed spin polarization of the current.

*Cell volume* X-ray diffraction (XRD) and transmission electron microscopy (TEM) demonstrate that the films grow epitaxially with the in-plane lattice parameter being dictated by the MgO substrate ($a_{\text{MnRuGa}} = \sqrt{2}a_{\text{MgO}}$) for all film thicknesses grown, while the out-of-plane lattice parameter $c$, depends strongly on the film thickness. This results in cell volumes much larger than those predicted by DFT; and their variation with film thickness cannot be explained.

*Magnetism* The measured magnetic moment as a function of Ru concentration is linear for $0.3 \leq x \leq 0.7$ with slope $dM/dx = 2$, suggesting that there is a spin gap at the Fermi level over an extended range of concentrations, in contradiction to the DFT results.

Here we address and resolve the conflict between experiment and theory. By applying a high-throughput approach based on the VASP implementation of DFT and the Perdew-Burke-Ernzerhof (PBE) functional, we have calculated the properties of 1221 Heusler phases containing Mn, Ru and Ga, that present different stoichiometry, magnetic order and site occupancy within the L2$_1$ and C1$_b$ symmetries. Other symmetries were excluded from the search. For each configuration we compute the enthalpy of formation, $\Delta H$, with respect to the lowest energy phase of each of the constituent elements, allowing us to compare the relative stability of the various configurations. Our results for the lowest energy structures are summarized in Table 1.

For the Mn$_2$RuGa composition, we find that the lowest energy structure corresponds to Mn occupying the inequivalent 4$a$, 4$c$ sites, Ga the 4$b$ and Ru taking the remaining 4$d$ site, consistent with literature. Cubic Mn$_2$Ga was found to have a positive enthalpy of formation of 0.54 eV f.u.$^{-1}$, making the compound unstable with respect to decomposition into its elementary phases. The symmetry of the stable D0$_{22}$ structure was excluded from our calculations. However, the most energetically favourable Mn$_2$Ga structure in the L2$_1$ phase, places Mn on the inequivalent 4$a$ and 4$c$ sites with Ga occupying the 4$b$ one. The structure remains cubic and the magnetic state is ferrimagnetic, consistent with experimental characterisation presented by Kurt et al. for thin films stabilized on a suitable substrate or a seed layer. We note that the formation of any half-Heusler in the Mn, Ru and Ga phase diagram is energetically unfavourable, so that we would not expect pure half-Heuslers to be a significant constituent of the films.

We note that the energy of the system can be lowered by forming Mn-deficient MnRu$_2$Ga or MnGa$_2$Ru (#1 and 2 in table 1). Given that the difference in formation enthalpy of these phases with respect to Mn$_2$RuGa (#3 in table 1) is only 0.14 eV f.u.$^{-1}$, we expect that actual samples will not form distinct polycrystalline phases, but instead display significant site disorder, particularly on the 4$a$ site, with a preference towards a lower Mn content. This was confirmed by laser-assisted inductively coupled mass spectrometry (ICPMS) measurements of the Mn-to-Ga ratio for a series of samples with varying Ru concentration, $x$. The ratio was observed to be in the 1.6-1.9 range, increasing with increasing film thickness.

In Fig. 2(a) we show scanning transmission electron microscopy (STEM) measurements of electron-transparent lamellae of Mn$_2$RuGa which indicate that there is little variation in either the in-plane or out-of-plane lattice constants throughout the film. The corresponding electron energy loss (EELS) spectra and line profiles are shown in Fig. 2(b). Alternating light and dark bands in dark-field images indicate slight compositional variations, especially in the layers closest to the surface. EELS measurements reveal that these bands correspond to layers of Mn enrichment and Ru depletion, suggesting a degree of phase segregation during growth, but not at the level of formation of half-Heuslers. We also note that the Ru concentration, $x$, decreases by about 20% from the interface with the substrate through the thickness of the film; to a lesser extent, the Mn concentration increases across the same range.

| #  | 4$a$ | 4$c$ | 4$b$ | 4$d$ | $\Delta H$ [eV] | $M$ [$\mu_B$] | c/a | Vol [Å$^3$] |
|----|------|------|------|------|---------------|-----|-----|----------|
| 1  | Mn   | Ru   | Ga   | Ru   | -1.11         | 2.18 | 1.0 | 56.33    |
| 2  | Ga   | Mn   | Ga   | Ru   | -0.99         | 2.92 | 1.0 | 55.83    |
| 3  | Mn   | Mn   | Ga   | Ru   | -0.97         | 0.07 | 1.2 | 55.88    |
| 4  | Mn   | Mn   | Ga   | Ru   | -0.52         | 4.66 | 1.0 | 55.01    |
| ...|      |      |      |      |               |      |      |          |
| 10 | Ga   | Mn   | Ga   | –    | 0.02          | 3.14 | 1.0 | 52.01    |
| 12 | Ru   | Mn   | Ga   | –    | 0.27          | 0.19 | 1.0 | 44.70    |
| 13 | Ru   | Mn   | Ga   | Ru   | 0.29          | 4.44 | 1.0 | 59.20    |
| 14 | –    | Mn   | Ga   | Ru   | 0.52          | 4.50 | 1.0 | 49.60    |
| 15 | Mn   | Mn   | Ga   | –    | 0.54          | 0.47 | 1.0 | 46.54    |
| ...|      |      |      |      |               |      |      |          |

*a* Magnetization quenched by the tetragonal distortion.

*b* Ferromagnetic Mn$_2$RuGa phase.

TABLE I: Calculated enthalpies of formation, $\Delta H$, for the most stable competing Heusler phases of the 1221 structural and magnetic Mn-Ru-Ga cells investigated. The configurations investigated are limited to the primitive 4-atom Heusler cell (3-atom for half-Heuslers).
In order to investigate the properties of low-Mn-content films we have performed supercell calculations where 1/3 of the Mn atoms at the 4a site are substituted with Ga. The Mn-Ga substitution simultaneously changes the lattice parameters, the magnetic properties and the electronic structure of the system. We find that the ionic charges of Mn and Ga are +2 and +1, respectively. Hence a one-atom Mn-Ga substitution leaves the system with one unbound electron, thus creating electronic doping. Below we describe in detail the properties of such Mn-deficient compounds.

**Lattice**  Electronic doping provides an explanation for the variation of the lattice parameter with film thickness. From the volume difference between the relaxed DFT structure and the corresponding experimental one and by using the bulk modulus $B_0$, we estimate the experimental electronic doping. The bulk modulus is calculated for Mn$_2$Ru$_x$Ga ($x = 0.0, 0.33, 0.50, 0.66$ and $1.0$) compounds by fitting the Murnaghan equation of state\cite{18, 19}. By using a simple model

$$n_{el} = \frac{B_0}{S_0} \left[ \frac{c}{a} \right]_{\exp} \left( \frac{a_{\exp}}{a_0} \right)^3 - 1 \right] ,$$

we can relate the experimentally observed lattice parameters to the electron doping level, $n_{el}$. In Eq.\(1\) $S_0$ is the rate of change of the excess pressure with electron doping, while $a_{\exp}$ and $a_0$ correspond to the experimental in-plane lattice constant and the relaxed theoretical lattice constant, respectively. This equation is easily derived under the assumption that the material is in mechanical equilibrium at the experimental lattice constant, due to the excess pressure provided by the Mn-Ga substitution, via the electron doping mechanism. Since we are comparing pressure differences, we ignore constant pres-
sure terms. In order to stabilise the experimental lattice parameters, including the observed $c/a > 1$, we find electron doping in the range $0.1 \text{ e.f.u.}^{-1}$ to $0.5 \text{ e.f.u.}^{-1}$, corresponding to a Mn/Ga ratio in the interval $1.4$ to $2.0$. The higher doping level occurs for the lower Ru concentrations, as shown in the inset of Fig. 6.

TEM imaging and spectroscopy clearly indicate that there are regions of high Mn content, and therefore regions of enhanced Ga content elsewhere in the sample. It is therefore reasonable to assume that films of different thicknesses will have a different electronic doping, which in turn alters the $c$-lattice parameter and does so uniformly throughout the sample.

**Magnetism** A key feature of a CFHM is the magnetically compensated ground state. In agreement with Ref. [12], we find that the magnetization calculated for MRG compounds, as a function of the Ru doping, differs from the experimental one (see Fig. 3). The discrepancy is two-fold: I) the slope of the magnetization with $x$ disagrees by a factor of 2, and II) there is no compensation of the magnetization around $x = 0.5$. These discrepancies are resolved if we take into account the effect of the Mn-Ga substitution on the magnetic properties. Ga defects introduce, in addition to the electronic doping, a change in the net magnetic moment per unit cell, of $-2 \mu_B$ per Mn substituted by Ga, which allows us to express the expected moment $M_{\text{EXP}}$ as

$$M_{\text{EXP}}(x) = M_{\text{DFT}}(x) - 2 \cdot n_{el}(x),$$

where $M_{\text{DFT}}$ is the theoretically calculated magnetic moment for a defect-free Mn$_2$Ru$_2$Ga compound.

The corrections given by Eqs. (1) and (2) have been applied for each value of $x$, and the results are summarised in Fig. 3. Notably, the presence of defects improves significantly the agreement between the experimental and theoretical magnetic moments, with the exception of concentrations around $x = 1$. A neutron diffraction study by Hori et al. [4] has shown that the magnetization of stoichiometric Mn$_2$RuGa ($x = 1$) is $\approx 1 \mu_B$, in good agreement with our calculations. This leads us to the conclusion that in the $x = 1$ limit there may be a substantial content of the Ru$_2$MnGa phase, which is known to be antiferromagnetic [1].

**Electronic Structure** Finally, we discuss the effect of the electronic doping on the degree of transport spin polarisation. In figure 4 we show the DOS and corresponding Boltzmann resistivity for Mn$_2$RuGa with $n_{el} = 0.4$ extra electrons per formula unit, corresponding to a Mn/Ga ratio of 1.6 as observed by ICPMS. The additional doping results in a transport spin polarization of $\approx 60\%$, which is twice as large as the one calculated for the original Mn$_2$Ru$_2$Ga compound. At a doping level of $n_{el} = 1.0$ the transport spin polarization becomes 100%. It is important to note that the calculations presented here do not take into account the effect of the disorder due to the Mn-Ga substitution on the transport properties. We anticipate that the presence of disorder may open further the spin gap, resulting in a cumulative effect where the disorder provides both the spin gap and the electron doping necessary for reinstating the half-metallicity. The improvement of spin-transport properties obtained by introducing disorder, has already been discussed by Chado et al. [20].

In conclusion, a sustained dialogue between experimental measurements and theoretical calculations have demonstrated that Mn$_2$Ru$_x$Ga can form a true CFHM. As a consequence we expect that it will become a cornerstone for future spintronics technology. By means of high-throughput calculations, we have shown that there are several competing phases in the Mn-Ru-Ga system; and that due to their small energy differences they exhibit a strong tendency towards site disorder, and a preference for reduced Mn content. This has all been confirmed by our experimental characterization of MRG thin films. Furthermore the low Mn content provides an electronic doping mechanism, pushing the system towards half-metallicity and improving the agreement between experiment and theory regarding the structural and magnetic properties of the system. Based on our calculations, complete transport spin polarisation can be achieved. We have shown that chemical composition, $c/a$ ratio, tendency to site-disorder and cell volume are all correlated. To achieve transport half-metallicity and zero net moment, a reduced Mn to Ga ratio of $\approx 1.4$ is required, as well as a Ru concentration of $\approx 0.7$. Fine-tuning of the position of the Fermi level in the spin gap can then be achieved through varying the $c/a$ ratio, which we have shown can be done by varying the film thickness.

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[1] H. Van Leuken and R. A. De Groot, Phys. Rev. Lett. 74, 1171 (1995).
[2] M. Hakimi, M. Venkatesan, K. Rode, K. Ackland, and J. M. D. Coey, J. Appl. Phys. 113, 17B101 (2013).
[3] L. Yang, B. Liu, F. Meng, H. Liu, H. Luo, E. Liu, W. Wang, and G. Wu, J. Magn. Magn. Mater. 379, 1 (2015).
[4] T. Hori, M. Akimitsu, H. Miki, K. Ohoyoama, and Y. Yamaguchi, Appl. Phys. A-Mater. 74, s737 (2002).
[5] S. Wurmehl, H. C. Kandpal, G. H. Fecher, and C. Felser,
J. Phys.-Condens. Mat. **18**, 6171 (2006).

6. I. Galanakis, P. Mavropoulos, and P. H. Dederichs, J. Phys. D Appl. Phys. **39**, 765 (2006).

7. E. Şaşioğlu, Phys. Rev. B **79**, 100406 (2009).

8. X. Hu, Adv. Mater. **24**, 294 (2012).

9. H. Kurt, K. Rode, P. Stamensov, M. Venkatesan, Y.-C. Lau, E. Fonda, and J. M. D. Coey, Phys. Rev. Lett. **112**, 027201 (2014).

10. N. Thiyagarajah, Y.-C. Lau, D. Betto, K. Borisov, J. M. D. Coey, P. Stamensov, and K. Rode, Appl. Phys. Lett. **106**, 122402 (2015).

11. D. Betto, N. Thiyagarajah, Y.-C. Lau, C. Piamonteze, M.-A. Arrio, P. Stamensov, J. M. D. Coey, and K. Rode, Phys. Rev. B **91**, 094410 (2015).

12. I. Galanakis, K. Özdoğan, E. Şaşioğlu, and S. Blügel, J. Appl. Phys. **116**, 033903 (2014).

13. I. Galanakis, P. H. Dederichs, and N. Papanikolaou, Phys. Rev. B **66**, 134428 (2002).

14. T. Timusk and B. Statt, Rep. Prog. Phys. **62**, 61 (1999).

15. http://www.materials-mine.com.

16. G. Y. Sun, J. Kürti, P. Rajczy, M. Kertesz, J. Hafner, and G. Kresse, J. Mol. Struc.-Theochem **624**, 37 (2003).

17. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).

18. C. L. Fu and K. M. Ho, Phys. Rev. B **28**, 5480 (1983).

19. F. D. Murnaghan, **30**, 244 (1944), PMC1078704.

20. S. Chadov, J. Kiss, and C. Felser, Adv. Funct. Mater. **23**, 832 (2013).