Compensated ferrimagnetic half metals (CFHMs) have an ordered spin state with no 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 polarized spin state allows switching of the magnetization via spin-transfer torque. The class of CFHMs was first envisaged by van Leuken and de Groot [1] in 1995, but despite significant effort [2–7] the goal of a CFHM has not been achieved. Half-metallic Heuslers have an ordered spin state with no net magnetic moment. As the number of valence electrons, $N_v$, is given by $N_v = 18$ for Mn$_2$Ga, $N_v = 25$ for Mn$_2$RuGa, and $N_v = 24$, where $N_v$ is the number of valence electrons. For Mn$_2$RuGa, $N_v = 25$, resulting in a net moment of $+1\mu_B$. Mn$_2$RuGa is expected to have a half-Heusler ($C_{1h}$) structure [13], with Mn on 4$a$, $4c$, and Ga on 4$b$ sites, thus leaving the 4$d$ site empty. In half-metallic Heuslers with the $C_{1h}$ structure, the magnetic moment $m$ is given by $m = N_v - 18$. For Mn$_2$Ga, $N_v = 17$ and hence $m = -1\mu_B$. The idea behind the Mn$_2$Ru$_{0.5}$Ga system, including magnetic compensation and the spin gap at the Fermi level, is to correct the magnetic moment, 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 a ferrimagnetic half metal with a compensation point close to room temperature.

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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 [17] implementation of DFT and the Perdew-Burke-Emzerhof (PBE) [18] 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 $L_2_1$ and $C1_b$ symmetries [19]. 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 I.

![Image](140202-2)

**FIG. 1.** (a) Spin resolved resistivity (green) and the corresponding density of states (DOS) (blue) calculated for the Mn$_2$Ru$_2$Ga. The data corresponding to the spin down channel are represented with negative values. (b) Calculated transport spin polarization.

TABLE I. Calculated enthalpies of formation $\Delta H$ for the most stable competing Heusler phases of the 1221 structural and magnetic (No. 4 for the Mn$_2$RuGa composition, we find that the lowest energy structure corresponds to Mn occupying the inequivalent 4$a$, 4$c$, 4$b$, sites, Ga the 4$b$, and Ru taking the remaining 4$d$ site, consistent with literature [4,9]. 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 favorable Mn$_2$Ga structure in the $L_2_1$ phase (No. 15) places Mn on the inequivalent 4$a$ and 4$c$ sites with Ga occupying the 4$b$ site. The structure remains cubic and the magnetic state is ferrimagnetic, consistent with experimental characterizations presented by Kurt et al. [9] 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 unfavorable, 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 Mn$_2$RuGa or Mn$_2$Ga$_2$Ru (No. 1 and No. 2 in Table I). Given that the difference in formation enthalpy of these phases with respect to Mn$_2$RuGa (No. 3 in Table I) 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 spectroscopy (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 [20].

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.

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 4$a$ 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 [21]. From the volume difference between the relaxed DFT structure and...
FIG. 2. Analytical electron microscopy analysis of the thin film (x = 1) composition. (a) High angle annular dark field (HAADF) image of a typical sample cross section, with the region where EELS data were acquired indicated by a white rectangle. In HAADF images, heavy elements appear brightest. (b) Elemental variations across the thin film stack, as measured by EELS. Data are normalized by setting the average composition to Mn₂GaRu. The dashed vertical lines indicate regions of Mn enrichment and Ru depletion, corresponding to darker features in the HAADF image.

The corresponding experimental one and by using the bulk modulus \( B_0 \), we estimate the experimental electronic doping. The bulk modulus is calculated for Mn₂RuGa (x = 0.0, 0.33, 0.50, 0.66, and 1.0) compounds by fitting the Murnaghan equation of state [22,23]. By using a simple model

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

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 \( a_{\text{expt}} \) 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 pressure terms. In order to stabilize the experimental lattice parameters, including the observed \( c/a > 1 \), we find electron doping in the range 0.1–0.5 e f.u. \(^{-1}\), corresponding to a Mn/Ga ratio in the interval 1.4–2.0. The higher doping level occurs for the lower Ru concentrations, as shown in the inset of Fig. 3.

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 twofold: (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

\[
 M_{\text{EXP}}(x) = M_{\text{DFT}}(x) - 2n_{el}(x), \tag{2}
\]

where \( M_{\text{DFT}} \) is the theoretically calculated magnetic moment for a defect-free Mn₂RuGa compound.

The corrections given by Eqs. (1) and (2) have been applied for each value of \( x \), and the results are summarized 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 Mn₂RuGa (x = 1)
is ≈ 1µB, 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 Ru2MnGa phase, which is known to be antiferromagnetic [4].

Electronic structure. Finally, we discuss the effect of the electronic doping on the degree of transport spin polarization. In Fig. 4 we show the DOS and corresponding Boltzmann resistivity for Mn2RuGa with nel = 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 ≈60%, which is twice as large as the one calculated for the original Mn2Ru, Ga compound. At a doping level of nel = 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. The stoichiometry has been shown to vary across the film as shown in Fig. 2, and we would therefore expect a variation of the electronic structure which will in turn reduce the spin gap [12]. However, the robustness of the experimentally observed spin polarization can only be rationalized if a wide enough disorder-induced transport spin gap exists at the Fermi level. Disorder introduces a smearing to the band picture, reducing conductivity in both spin channels through Anderson localization [24]. Localization of the states originates at the band edge, leaving the center of the band delocalized [25]. In MRG the Fermi level lies at the edge of the majority spin band, whereas for the minority it is at the band center. We would therefore expect that localization to affect the conductivity of the majority spin channel more than the minority, resulting in an increased transport spin polarization. Chadov et al. have demonstrated that this mechanism is applicable in the Mn3−xCoxGa system [26].

Ideal half metallicity exists only in the zero-temperature limit, and in the absence of spin-orbit interaction. Compensation for practical materials under ambient conditions occurs at a specific temperature, which can be tuned by composition and strain, while maintaining the Fermi level in the spin gap. This can be achieved because, unlike an antiferromagnet, the two magnetic sublattices have different temperature dependences [7,11].

In conclusion, a sustained dialogue between experimental measurements and theoretical calculations has demonstrated that Mn2Ru, Ga can form a true CFHM. As a consequence, we expect that it may 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 polarization can be achieved.

We have shown that the 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 ≈1.4 is required, as well as a Ru concentration of ≈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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