Taking Advantage of Gold’s Electronegativity in \( R_4Mn_3-xAu_{10+x} \) (\( R = \text{Gd or Y}; 0.2 \leq x \leq 1 \))

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Taking Advantage of Gold's Electronegativity in R4Mn3–xAu10+x (R = Gd or Y; 0.2 ≤ x ≤ 1)

Abstract
Ternary $R_4Mn_{3-x}Au_{10+x}$ (R = Gd or Y; 0.2 ≤ x ≤ 1) compounds have been synthesized and characterized using single-crystal X-ray diffraction. The structure is a ternary variant of orthorhombic Zr$_7$Ni$_{10}$ (oC68, space group Cmca) and is isostructural with Ca$_4$In$_3$Au$_{10}$. The structure contains layers of Mn-centered rectangular prisms of gold (Mn@Au$_8$), interbonded via Au atoms in the b-c plane, and stacked in a hexagonal close packed arrangement along the a direction. These layers are bonded via additional Mn atoms along the a direction. The rare-earth metals formally act as cations and fill the rest of the space. The structure could also be described as sinusoidal layers of gold atoms, which are interconnected through Au–Au bonds. The magnetic characteristics of both compounds reveal the presence of nearly localized Mn magnetic moments. Magnetization $M$ measurements of $Y_4Mn_{2.8}Au_{10.2}$ versus temperature $T$ and applied magnetic field $H$ demonstrate the dominance of antiferromagnetic (AFM) interactions in this compound and indicate the occurrence of noncollinear AFM ordering at $T_{N1} = 70$ K and a spin reorientation transition at $T_{N2} = 48$ K. For the Gd analogue Gd$_4Mn_{2.8}Au_{10.2}$, the $M(H,T)$ data instead indicate the dominance of ferromagnetic interactions and suggest a ferrimagnetic transition at $T_C \approx 70$ K for which two potential ferrimagnetic structures are suggested. Linear muffin-tin orbital calculations on the stoichiometric composition “$Y_4Mn_3Au_{10}$” using the local spin density approximation indicate a ~1 eV splitting of the Mn 3d states with nearly filled majority spin states and partially filled minority spin states at the Fermi level resulting in approximately four unpaired electrons per Mn atom in the metallic ground state. The crystal orbital Hamilton population analyses demonstrate that ~94% of the total Hamilton populations originate from Au–Au and polar Mn–Au and Y–Au bonding.

Disciplines
Atomic, Molecular and Optical Physics | Other Astrophysics and Astronomy | Other Chemistry | Physical Chemistry

Comments
Taking Advantage of Gold’s Electronegativity in $R_4Mn_{3−x}Au_{10+x}$ ($R = \text{Gd or Y}; 0.2 \leq x \leq 1$)

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ABSTRACT: Ternary $R_4Mn_{3−x}Au_{10+x}$ ($R = \text{Gd or Y}; 0.2 \leq x \leq 1$) compounds have been synthesized and characterized using single-crystal X-ray diffraction. The structure is a ternary variant of orthorhombic $ZrN_{10}$ (c$6\bar{3}$, space group $Cmca$) and is isostructural with $Ca_4In_7Au_{10}$. The structure contains layers of Mn-centered rectangular prisms of gold $(\text{Mn@Au}_8)$, interbonded via Au atoms in the $b$-$c$ plane, and stacked in a hexagonal close packed arrangement along the $a$ direction. These layers are bonded via additional Mn atoms along the $a$ direction. The rare-earth metals formally act as cations and fill the rest of the space. The structure could also be described as sinusoidal layers of gold atoms, which are interconnected through Au–Au bonds. The magnetic characteristics of both compounds reveal the presence of nearly localized Mn magnetic moments. Magnetization $M$ measurements of $Y_4Mn_{3−x}Au_{10+x}$ versus temperature $T$ and applied magnetic field $H$ demonstrate the dominance of antiferromagnetic (AFM) interactions in this compound and indicate the occurrence of noncollinear AFM ordering at $T_{N1} = 48$ K. For the Gd analogue $Gd_4Mn_{3−x}Au_{10+x}$, the $M(H,T)$ data instead indicate the dominance of ferromagnetic interactions and suggest a ferrimagnetic transition at $T_c \approx 70$ K for which two potential ferrimagnetic structures are suggested. Linear muffin-tin orbital calculations on the stoichiometric composition $Y_4MnAu_{10}^+$ using the local spin density approximation indicate a ~1 eV splitting of the Mn 3d states with nearly filled majority spin states and partially filled minority spin states at the Fermi level resulting in approximately four unpaired electrons per Mn atom in the metallic ground state. The crystal orbital Hamilton population analyses demonstrate that ~94% of the total Hamilton populations originate from Au–Au and polar Mn–Au and Y–Au bonding.

INTRODUCTION

Exploratory syntheses have been significant in the discovery of new crystalline intermetallic phases and the revelation of their chemical and physical properties.1,2 Polar intermetallic phases, in particular, are generally obtained from reactions among (1) an electropositive alkali (A) or alkaline-earth (Ac) metal, (2) a relatively electronegative late transition metal, and (3) a main group p metal or metalloid. Inclusions of gold in these systems have led to significant gains in terms of new structures and bonding patterns, evidently because of substantial relativistic effects3 that enhance gold’s bonding to itself and other late post-transition metals. Several gold-based ternary compounds with unusual bonding patterns have been discovered in $A/\text{Ac–Au–Tr}/\text{Di}$ systems ($\text{Tr} = \text{Ga or In}; \text{Di} = \text{Zn or Cd}$).4–15 For example, a ternary phase containing a network of condensed Cd tetrahedral stars was found for $Na_4Cd_4Au$ in the Na–Au–Cd system,14 whereas two tunnel-like compounds with somewhat diffuse but locally ordered cation distributions have been discovered in the Na–Au–Zn system.15 The comparatively more tightly bound alkaline-earth or rare-earth ($R$) metals usually produce significant modifications, in particular providing higher-symmetry phases with stronger cation bonding.16 Several ternary examples of related rare-earth metal analogues, most of which are rich in rare-earth metals, have also been reported.17–19

Exploration of new intermetallic chemistry by incorporating the 3d transition element, Mn, with several active metal–Au mixtures led to the discovery of a rhombohedral, intergrown cluster compound $Y_3\text{MnAu}_{20}$.20 This compound contains a 2:1 intergrowth of $\text{Mn@Au}_{8}$ and $\text{Au@Y}_6$ polyhedra arranged in a cubic-close-packed array along the $c$ axis and the magnetic properties suggest noncollinear antiferromagnetic order below 75 K. Further exploration in $R_4\text{Mn–Au}$ ($R = \text{Gd or Y}$) systems led to the discovery of $R_4Mn_{3−x}Au_{10+x}$ compounds. Here we report the synthesis, structure, bonding, and magnetic properties of $R_4Mn_{3−x}Au_{10+x}$ ($R = \text{Gd or Y}; 0.2 \leq x \leq 1.0$).

EXPERIMENTAL SECTION

Syntheses. All reactants and products were handled inside a glovebox filled with dry $N_2$ ($\leq 0.1$ ppm of $H_2O$ by volume). Starting...
materials for the syntheses were Y or Gd (99.99%, Micron Metals), Mn (99.99%, Micron Metals), and Au (99.99%, BASF). The weighed reactants (\( \approx 0.5 \text{ g total} \)) were arc-melted two or three times under a dynamic argon atmosphere, turning the pellet each time, to obtain a well-homogenized sample (weight loss <1%) and then sealed inside Ta ampules that were subsequently sealed in evacuated silica jackets. The arc-melted samples were annealed at 1020°C for 3–4 days, then slowly cooled at a rate of 10 °C/h to 900 °C, and finally quenched in water. Single crystals of Gd\(_4\)Mn\(_3\)Au\(_{10.2}\) were first found from a loading of “Gd\(_{x}\)Mn\(_{9-x}\)Au\(_x\)”, and later, single-phase polycrystalline samples, according to X-ray powder diffraction (Figure S1 of the Supporting Information), were prepared according to the structurally refined composition by arc-melting the required amounts of Gd (or Y), Au, and Mn followed by annealing as discussed above. The compounds have metallic lustre, and the powder is visibly stable in air at room temperature for at least a few days. Reactions in which Mn have metallic lustre, and the powder is visibly stable in air at room temperature for at least a few days. Reactions in which reactants (Mn (99.99%, Micron Metals), and Au (99.99%, BASF). The weighed materials for the syntheses were Y or Gd (99.995%, Ames Laboratory), and Cu K\( \alpha \) radiation (\( \lambda = 1.54059 \) Å). The well-ground powder samples were dispersed between two acetate films with the aid of a small amount of grease and enclosed in a STOE sample holder. Complete listings of lattice parameters for Gd\(_4\)Mn\(_{2.8}\)Au\(_{10.2}\) and Gd\(_4\)Mn\(_{3}\)Au\(_{10.2}\) were included.27 The Wigner-Seitz radii of the spheres were assigned from single-crystal data used these values.

Results and Discussion

Structure. The title compounds are new ternary phases in the R–Mn–Au system (R = Gd or Y), in which only the R\(_4\)Mn\(_{3-x}\)Au\(_{10.2}\) compounds are isostructural with Ca\(_4\)In\(_3\)Au\(_{10} \) (ref 7) and are ternary variants of Zr\(_2\)Ni\(_{10}\).30 The series Gd\(_4\)Mn\(_{3-x}\)Au\(_{10.2}\) for which \( x \approx 0.2, 0.25, 0.5, 0.6, 1.0 \) and Y\(_4\)Mn\(_{5-x}\)Au\(_{10.2}\) (\( x \approx 0.2, 0.3, 0.4 \)) are given in Tables S1 and S2 of the Supporting Information, respectively. The refinements were accomplished using WinPOw22 and all the distance calculations from single-crystal data used these values. Single-crystal diffraction data sets were collected at room temperature over a 2\( \theta \) range from \( \sim 6^\circ \) to \( \sim 65^\circ \) with 0.5° scans in \( \omega \) and 10 s per frame exposures with the aid of a Bruker SMART CCD diffractometer equipped with an image plate and Cu Ka1 radiation (\( \lambda = 0.71073 \) Å). The data showed an orthorhombic C-centered lattice, and the intensity statistics indicated a centrosymmetric space group. The reflection intensities were integrated with APEX II in the SMART software package.23 Empirical absorption corrections were employed using SADABS.24 Space group Pnma (No. 64) of the structures was determined with the help of XPREP and SHELXLT version 6.1.25 The structure was determined by direct methods and subsequently refined on \( {\text{|P|}} \) with combinations of least-squares refinements and difference Fourier maps.

Seven independent atomic positions were obtained by direct methods, three of which are assigned as Au1, Au2, and Au3 sites, two as R1 and R2 sites, and two as Mn1 and Mn2 sites. However, the Mn sites indicate larger observed electron densities and smaller displacement parameters, and hence, those were subsequently refined as mixed Mn/Au sites. The refinements of Gd\(_4\)Mn\(_{3-x}\)Au\(_{10.2}\) converged to \( R_{\text{free}} = 0.0488 \) and \( R_{\text{wp}} = 0.0734 \) for all data with a goodness of fit of 0.996 and maximal residuals of 3.4 and \( \pm 2.5 \text{ e/Å}^3 \) that were 0.8 and 1.1 Å from Au1 = 3.075 Å, and Au2 = 3.144 Å). These distances are given in Tables S1 and S2 of the Supporting Information, respectively. The corresponding atomic positions are listed in Tables S3 and S4 of the Supporting Information, respectively. The cif files are also provided in the Supporting Information.

Electronic Structure Calculations. Electronic structure calculations on a hypothetical model compound, "Y\(_4\)Mn\(_{3-x}\)Au\(_{10.2}\)" were performed self-consistently using the tight-binding linear-muffin-tin-orbital (TB-LMTO) method within the atomic sphere approximation (ASA).26 In addition, the simplest (collinear) model that would allow the observed antiferromagnetic coupling was employed, and that is in space group Pnma, in which each Mn site is split into two independent sites (Mn1 from 8i into two distinct 4g sites; Mn2 from 4a into 2a and 2c sites) and the resulting pairs are each assigned opposite spin orientations. The exchange and correlation were treated in the local spin density approximation (LSDA). Scalar relativistic corrections were included.27 The Wigner-Seitz radii of the spheres were assigned automatically so that the overlapping potentials would be the best possible approximation to the full potential.28 The radii (Å) were as follows: Y1 = 1.87, Y2 = 1.87, Y3 = 1.94, Y4 = 1.94, Mn1 = 1.54, Mn2 = 1.54, Mn3 = 1.56, Mn4 = 1.56, Au1 = 1.59, Au2 = 1.59, Au3 = 1.57, Au4 = 1.57, Au5 = 1.50, and Au6 = 1.50. No additional empty spheres were needed subject to an 18% overlap restriction between atom-centered spheres. Basis sets of Y 5s, 4d; Mn 4s, 4p, 3d; and Au 6s, 6p, 4f (downdfolded orbitals in parentheses) were employed, and the tetrahedron method using an 8 \( \times \) 8 \( \times \) 8 mesh of \( k \) points was applied to perform the reciprocal space integrations. For bonding analysis, the crystal orbital Hamilton populations (COHPs)29 of all filled electronic states for selected atom pairs were calculated. The weighted integration of COHP curves of these atom pairs up to the Fermi energy (\( E_F \)) provides ICOHP values, i.e., total (integrated) Hamilton populations (Table S and Table SS of the Supporting Information), which are approximations of relative bond strengths. The COHP analyses provide the contributions of the covalent parts of particular pairwise interactions to the total bonding energy of the crystal.
Table 1. Crystal Data and Structural Refinement Parameters for Orthorhombic Gd₄Mn₃₋ₓAuₓ (x = 0.2, 0.25, 0.6, or 1.0)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Gd₄Mn₂₋ₓAuₓ⁺ₓ(1)</th>
<th>Gd₄Mn₂₋ₓAuₓ⁺ₓ(2)</th>
<th>Gd₄Mn₂₋ₓAuₓ⁺ₓ(3)</th>
<th>Gd₄Mn₂₋ₓAuₓ⁺ₓ(4)</th>
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<td>Empirical formula</td>
<td>Gd₂Mn₅Au₄⁺ₓ</td>
<td>Gd₂Mn₅Au₄⁺ₓ</td>
<td>Gd₂Mn₅Au₄⁺ₓ</td>
<td>Gd₂Mn₅Au₄⁺ₓ</td>
</tr>
<tr>
<td>Formula weight (g)</td>
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<td>2803.247</td>
<td>2851.537</td>
<td>2916.87</td>
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<td>Cmca, 4</td>
<td>Cmca, 4</td>
<td>Cmca, 4</td>
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<tr>
<td>Density (g cm⁻³)</td>
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<td>13.58</td>
<td>13.99</td>
<td>14.32</td>
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<tr>
<td>Absorption coefficient (mm⁻¹)</td>
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<td>3.00–30.00</td>
<td>3.00–30.04</td>
<td>3.02–30.08</td>
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<td>Index ranges</td>
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<td>−19 ≤ h ≤ 18; −10 ≤ k ≤ 13; −14 ≤ l ≤ 14</td>
<td>−18 ≤ h ≤ 16; −12 ≤ k ≤ 13; −14 ≤ l ≤ 11</td>
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<td>No. of reflections collected</td>
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<td>6733</td>
<td>1030</td>
<td>7740</td>
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<tr>
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<td>1014/47</td>
<td>1030/47</td>
<td>1320/47</td>
</tr>
<tr>
<td>Goodness of fit on F²</td>
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<td>0.994</td>
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<tr>
<td>R indices [I &gt; 2σ(I)]</td>
<td>R₁ = 0.0326; wR₂ = 0.0663</td>
<td>R₁ = 0.0344; wR₂ = 0.0692</td>
<td>R₁ = 0.0317; wR₂ = 0.0724</td>
<td>R₁ = 0.0361; wR₂ = 0.0659</td>
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<tr>
<td>Largest difference peak and hole (e Å⁻³)</td>
<td>3.46 (0.81 Å from Au3) and −2.48 (1.16 Å from Au3)</td>
<td>3.62 (0.93 Å from Au3) and −3.19 (1.77 Å from Mn5)</td>
<td>4.31 (0.74 Å from Au1) and −2.87 (0.70 Å from Au3)</td>
<td>3.16 (1.9 Å from Au1) and −3.63 (1.47 Å from Au2)</td>
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</tbody>
</table>

Table 2. Crystal Data and Structural Refinement Parameters for Orthorhombic Y₄Mn₃₋ₓAuₓ (x = 0.2, 0.3, or 0.4)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Y₄Mn₃₋ₓAuₓ⁺ₓ(1)</th>
<th>Y₄Mn₃₋ₓAuₓ⁺ₓ(2)</th>
<th>Y₄Mn₃₋ₓAuₓ⁺ₓ(3)</th>
<th>Y₄Mn₃₋ₓAuₓ⁺ₓ(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>Y₄Mn₃Au₄⁺ₓ</td>
<td>Y₄Mn₃Au₄⁺ₓ</td>
<td>Y₄Mn₃Au₄⁺ₓ</td>
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<td>Formula weight (g)</td>
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<td>Space group, Z</td>
<td>Cmca, 4</td>
<td>Cmca, 4</td>
<td>Cmca, 4</td>
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<tr>
<td>Density (g cm⁻³)</td>
<td>12.62</td>
<td>13.188</td>
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<td>Absorption coefficient (mm⁻¹)</td>
<td>12.62</td>
<td>13.188</td>
<td>13.237</td>
<td>13.075</td>
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<td>Goodness of fit on F²</td>
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<td>Largest difference peak and hole (e Å⁻³)</td>
<td>4.29 (0.90 Å from Au1) and −4.43 (1.41 Å from Au1)</td>
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<td>4.84 (0.92 Å from Au3) and −4.68 (0.79 Å from Au3)</td>
<td>4.84 (0.92 Å from Au3) and −4.68 (0.79 Å from Au3)</td>
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</table>
Table 3. Atomic Coordinates, Wycko Positions, Site Point Symmetries, Occupancies, and Isotropic Equivalent Displacement Parameters for Crystals 1–4 [Gd₄Mn₂₋₇₈(1)Au₁₀₋₂₂(1)/₁₉₀₂₋₆₂(₁ r) and Gd₄Mn₁₉₈(1)Au₁₁₋₂₀(1)r, respectively]¹

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<th>atom</th>
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Parameters for crystals 1–4 are listed in sequence. M denotes a Mn/Au mixture. Ueq is defined as one-third of the trace of the orthogonalized Uij tensor.

Table 4. Atomic Coordinates, Wycko Positions, Site Point Symmetries, Occupancies, and Isotropic Equivalent Displacement Parameters for Crystals 1–3 [Y₄Mn₂₋₇₈(1)Au₁₀₋₂₂(1)/₁₉₀₂₋₆₂(₁ r) and Y₄Mn₁₉₈(1)Au₁₁₋₂₀(1)r, respectively]¹

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Parameters for crystals 1–3 are listed in sequence. M denotes a Au/Mn mixture. Ueq is defined as one-third of the trace of the orthogonalized Uij tensor.
sinusoidal layer perspective between Zr$_7$Ni$_{10}$ and R$_4$Mn$_{3-x}$Au$_{10+x}$ (R = Y or Gd) compounds could be due to strong heteroatomic Mn−Au and Gd−Au bonding in the latter cases.

In the aristotypic Zr$_7$Ni$_{10}$ (ref 30), the environments of the four independent Zr atoms are quite different; namely, each Zr1 is surrounded by 11 Ni atoms, Zr3 by 10, and Zr2 and Zr4 each by eight Ni atoms, implying that Zr1 and Zr3 are located in the larger cavities. These size differences could account for Gd atoms occupying the Zr1 and Zr3 sites, whereas the smaller Mn atoms occupy the Zr2 and Zr4 sites in Gd$_4$Mn$_{3-x}$Au$_{10+x}$, an outcome that is consistent with relative Gd and Mn metallic radii (CN = 12; Gd, 1.970 Å; Mn, 1.579 Å). Therefore, Mn atoms have two crystallographic sites (4$a$ and 8$e$) in this compound, in which the 4$a$ (Mn2) site prefers to accommodate Mn whereas the 8$e$ site (Mn1) is occupied by a mixture of Mn and Au.

Panels a−d of Figure 2 show the nearest-neighbor environments of Mn1, Mn2, Gd1, and Gd2, respectively. Gd1 is surrounded by 11 Au and four Mn atoms in a polyhedron with a vertical mirror plane perpendicular to the $a$ axis that contains the Au3−Au3 bond, whereas Gd2 is surrounded by 10 Au and four Mn atoms that define a polyhedron with a vertical 2-fold rotation axis along the $a$ axis that bisects the Au3−Au3 bond. Mn1 atoms are surrounded by eight Au and six Gd neighbors, whereas Mn2 atoms are also surrounded by eight Au atoms but only four electropositive Gd atoms. The greater number of electropositive Gd neighbors surrounding the Mn1 (8$e$) sites could be the reason for its preferential occupation by a mixture of Mn and Au atoms.

To understand the magnetic properties of these ternary phases, it is important to identify the Mn and Gd/Y sublattices and their chemical environments. There are two distinct Mn sites in the structure, that form slightly distorted tracedge-shared square pyramids along the $b$ and $c$ directions with Mn1 (Mn/Au) sites forming a distorted square net and Mn2 sites serving as apical atoms, as shown in Figure 3a. The Mn−Mn distances range from 4.810(2) to 5.031(2) Å, distances much longer than those of typical covalent or metallic Mn−Mn.
moments of 3.90 and 3.85. ASA calculations give zero-temperature ordered magnetic completely spin-polarized with an energy difference between the majority and minority spin states. The LMTO calculations for an AFM model of Y₄MnAu₁₀⁺ indicate a moment on Mn (3.9 e) below a t₂g set (dₓ²−ᵧ² and d₃z²−r²). The distortion of the cubic geometry further breaks the degeneracy of the eₙ orbitals; according to a simple molecular orbital calculation on Mn@Au₈ (C₂v point symmetry) using extended Hückel theory (Figure S4 of the Supporting Information), the splitting is ~70 meV with the dₓ²−r² orbital lower in energy. It is this dₓ²−r² orbital of the minority spin states that is occupied and leads to the smaller net moment at Mn. The magnetic measurements, which are discussed in a subsequent section, also indicated a moment on Mn smaller than that expected for high-spin Mn.

Chemical bonding analysis of the AFM model of 'Y₄MnAu₁₀⁺' reveals several interesting features, which can be judged from a combination of DOS and COHP curves (Figure 4), as well as the integrated crystal orbital Hamilton population (ICOHP) data (Table S5). The important bond distances and the average ICOHP values for each bond type and their percent contributions to the total polar–covalent bonding per unit cell are listed in Table 5 and Table S5 of the Supporting Information. The average individual homoatomic Au–Au and heteratomic Mn–Au orbital interactions have −ICOHP values, 1.14 and 1.13 eV, respectively (Table S5), larger than those of all other contacts. The Y–Au interactions, however, are quite significant because they make up the largest contribution among all bonds within the unit cell (by a factor of almost 2 with respect to Au–Au and Mn–Au contacts), although the average individual −ICOHP value (0.71 eV) is smaller than these other averages; Y–Au bonds make a total contribution of 34% per unit cell. The bonding contributions of Mn–Au and Au–Au contacts are 31 and 28%, respectively, making heteroatomic polar Mn–Au and Y–Au bonding a dominant contribution to the total bonding energy. Y–Au bonding arises largely from interactions between Y 5s, 4d and Au 6s, 5d orbitals, whereas Mn–Au bonding comes from Mn 4s and 4p orbitals. It should be noted that Mn 4s and 4p orbitals participate significantly in bonding with gold and yttrium, whereas the different spin states of Mn 3d orbitals show opposing tendencies: the majority spin states, which are fully occupied, are well localized, and the minority spin states, which are mostly empty, are broadened via Y–Mn and Mn–Au interactions.

**Electronic Structure and Chemical Bonding.** Panels a–d of Figure 4 show the total electronic density of states (DOS) along with individual atom and orbital projections of stoichiometric \( Y₄MnAu₁₀⁺ \) obtained from tight-binding LMTO-ASA calculations using the LSDA (both majority and minority spin states are combined within the diagrams). The calculations were conducted for an AFM model of \( Y₄MnAu₁₀⁺ \) in space group Pmna. The COHP curves for each pairwise interaction as a function of energy are shown in Figure 4c. The Fermi energy, \( E_F \), indicated by the dotted vertical line, lies in a nonzero DOS region, ~12 states/eV of formula unit (f.u.) for both spin directions, indicating metallic character of the compound. Gold 5d states lie below ~2 eV and participate in Au–Au bonding as well as Mn–Au and Y–Au bonding. Manganese 3d states are completely spin-polarized with an energy difference of ~1 eV between the majority and minority spin states. The LMTO–ASA calculations give zero-temperature ordered magnetic moments of 3.90 and 3.85 μB for Mn1 and Mn2, respectively. The magnetic moments for other atoms are 0.05, 0.00, 0.02, 0.03, and 0.00 μB for Y1, Y2, Au1, Au2, and Au3, respectively. A significant fraction of the Y 4d states are present near and above \( E_F \), indicating the relative cationic nature of Y in these compounds. The values of the magnetic moment for Mn occur in the range, ~5 to 7 d states lie below \( E_F \), indicated by the dotted vertical line, lies in a nonzero DOS region, ~12 states/eV of formula unit (f.u.) for both spin states, which are fully occupied, are well localized, and the minority spin states, which are mostly empty, are broadened via Y–Mn and Mn–Au interactions.

**Magnetic Properties.** The temperature dependencies of the zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities \( \chi \equiv M/H \) of polycrystalline \( Y₄MnAu₁₀⁺ \) are...
shown in Figure 5a. The χ(T) data show a kink that we interpret as indicating an antiferromagnetic (AFM) transition at $T_{N1} = 70(1)$ K and exhibit a cusp at $T_{N2} = 48(1)$ K, suggesting the occurrence of an AFM spin reorientation transition at this temperature. The ZFC and FC χ(T) data nearly overlap with each other except below 70 K, where the data show a weak divergence (Figure 5a), confirming that the transitions at $T_{N1}$ and $T_{N2}$ are long-range AFM ordering transitions. The slight hysteresis below $T_{N1}$ is probably due to AFM domain wall effects.

The temperature dependence of χ of Y$_4$Mn$_2$Au$_{10.2}$ above $T_{N1}$ in the temperature range of 125−350 K was found to follow a Curie-Weiss (CW) law

$$\chi(T) = \chi_0 + \frac{C}{T - \theta_p}$$

where C is the Curie constant, $\theta_p$ is the Weiss temperature, and $\chi_0$ is a temperature-independent contribution to χ. The fitted parameters are listed in Table 6, and the fit is shown as the solid black curve in the inset of Figure 5a. The value of the effective paramagnetic moment per Mn atom ($\mu_{\text{eff Mn}}$) is estimated from the Curie constant to be $5.4(2) \mu_B/\text{Mn}$.

The observed CW T dependence of χ and the large value of $\mu_{\text{eff Mn}}$ suggest a local-moment character for the Mn atoms in the compound.

From Table 6, the Weiss temperature is $\theta_p = -22$ K and $T_{N1} = 70$ K. We take the ratio to obtain $f = \theta_p/T_{N1} = -0.31$. This value is different from the value of $-1$ obtained for an AFM system with only nearest-neighbor interactions with the same value. We discuss the observed value of f within the Weiss molecular field theory (MFT) of identical crystallographically equivalent localized spins interacting by the Heisenberg exchange Hamiltonian $\mathcal{H} = \sum_{ij} J_{ij} S_i S_j$ where each spin pair is only counted once, a positive $J_{ij}$ corresponds to an AFM interaction, and a negative $J_{ij}$ corresponds to a ferromagnetic (FM) interaction. Within MFT, $\theta_p$ and $T_N$ are given by $-\langle S(S+1)/3k_B \rangle \sum_{ij} J_{ij} \cos \theta_p$ and $-\langle S(S+1)/3k_B \rangle \sum_{ij} J_{ij} \cos \theta_p$ respectively. The value of $f$ is therefore $f = \theta_p/T_{N1} = (\sum J_{ij})/(\sum J_{ij} \cos \theta_p)$, where the sums are over all neighboring spins $j$ of a given spin $i$ and $\theta_p$ is the angle between spins $S_i$ and $S_j$ in the AFM-ordered magnetic structure. In an AFM with equal nearest-neighbor interactions, $\theta_p/T_{N1} = 1$.

The temperature dependence of $\chi$ of Y$_4$Mn$_2$Au$_{10.2}$ above $T_{N1}$ in the temperature range of 125−350 K was found to follow a Curie-Weiss (CW) law

$$\chi(T) = \chi_0 + \frac{C}{T - \theta_p}$$

where C is the Curie constant, $\theta_p$ is the Weiss temperature, and $\chi_0$ is a temperature-independent contribution to χ. The fitted parameters are listed in Table 6, and the fit is shown as the solid black curve in the inset of Figure 5a. The value of the effective paramagnetic moment per Mn atom ($\mu_{\text{eff Mn}}$) is estimated from the Curie constant to be $5.4(2) \mu_B/\text{Mn}$.

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The parameters listed are AFM transition temperature $T_{N1}$, ferrimagnetic transition temperature $T_C$, the Curie constant per mole of formula units ($C$), the Curie constant per mole of Mn atoms ($C_{Mn}$), the effective paramagnetic moment per formula unit ($\mu_{eff}$), and the effective paramagnetic moment per Mn atom ($\mu_{eff\,Mn}$). The Curie constant and effective magnetic moment for $Y$ are considered to be zero.

**Table 6. Parameters Obtained from the Analysis of Magnetic Susceptibility $\chi(T)$ Data of $R_2Mn_2Au_{10.2}$ ($R = Y$ and Gd)**

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<th>$Gd_2Mn_2Au_{10.2}$</th>
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<td>$T_C = 70(4)$</td>
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<tr>
<td>$\mu_{eff,Mn}$ (amu$\mu_B$/Mn)</td>
<td>$5.4(1)$</td>
<td></td>
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</table>

The listed parameters are AFM transition temperature $T_{N1}$, ferrimagnetic transition temperature $T_C$, the Curie constant per mole of formula units ($C$), the Curie constant per mole of Mn atoms ($C_{Mn}$), the effective paramagnetic moment per formula unit ($\mu_{eff}$), and the effective paramagnetic moment per Mn atom ($\mu_{eff\,Mn}$). The Curie constant and effective magnetic moment for $Y$ are considered to be zero.

The magnetization versus applied magnetic field $M(H)$ isotherm measured at 300 K shows that $M$ is proportional to $H$ for $0 \leq H \leq 5.5$ T (Figure 5a), a behavior typical for local-moment systems in the paramagnetic state. The $M(H)$ isotherm at 50 K is also approximately linear, which is probably a result of a low-anisotropy field at the temperature $T_{N1} = 70$ K, together with polycrystalline averaging of the anisotropic noncollinear AFM response. However, the $M(H)$ isotherm at $T = 1.8$ K is not further discussed here.

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The magnetization and magnetic susceptibility data for Gd₄Mn₂Au₁₀ suggest a ferrimagnetic structure below the ferrimagnetic Curie temperature Tₑ = 70 K in which the Gd spins are aligned antiferromagnetically with no net magnetization at T = 0, but the Mn spins 5/2 are aligned ferromagnetically, giving rise to the strong negative curvature and saturation in M(H) at low T. Thus, the proposed character of the Mn magnetic ordering changes from AFM to FM in a similar compound, Gd₄Mn₂Au₁₀. Alternatively, the Mn spins could align antiferromagnetically, but with both Gd spins on one sublattice and one Gd spin on the other sublattice aligned ferromagnetically, which are in turn aligned antiferromagnetically with the second Gd spin on the second Gd sublattice, again resulting in a saturation moment of ~14 μᴮ/_'.$f$. Spectroscopic measurements are needed to test these hypotheses.

The similarity of the values of Tᴺ in Y₄M₃Au₁₀.2 and Tₑ in Gd₄Mn₂Au₁₀.2 is likely a coincidence. The Weiss temperatures in the two compounds are AFM and FM, respectively, demonstrating that the dominant interactions in the two compounds are AFM and FM, respectively. Furthermore, we infer that they have different magnetic structures at low temperatures that reflect this difference in interactions. A challenge for the future is to develop a microscopic theoretical explanation for these divergent properties of the two compounds.

### CONCLUSIONS

In these studies, we have discovered a R₄M₃₋ₓAuₓ₀₊₀ (R = Y or Gd) series of compounds that are isotypic with orthorhombic Ca₄In₃Au₁₀ and are ternary variants of Zr₇Ni₁₀. These compounds are attracting interest because of the combination of gold’s large relativistic effect on bonding and the magnetic nature of the Mn. Both effects are evident from the presence of strong polar bonds and magnetic behavior in these compounds.

Magnetic measurements suggest dominant AFM interactions and noncollinear AFM ordering for Y₄M₃Au₁₀ below 70 K. On the other hand, the magnetic data for the Gd analogue suggest dominant FM interactions and ferrimagnetic ordering below approximately the same temperature of 70 K are inferred, where the Gd spins are antiferromagnetically aligned, with the Mn spins giving rise to the ferrimagnetic component. An alternative ferrimagnetic structure contains three of the four Gd spins per f.u. aligned ferromagnetically, which are in turn aligned antiferromagnetically with the remaining Gd spin per f.u.; in this scenario, the Mn spins are assumed to align antiferromagnetically. It would be interesting to test these hypotheses about the different magnetic structures of these two related compounds via spectroscopic measurements such as neutron diffraction measurements for the Y compound and Gd Mössbauer spectroscopic measurements for the Gd compound.

### ASSOCIATED CONTENT

3 Supporting Information

Tables of lattice dimensions of Gd₄M₃₋ₓAuₓ₀₊₀ (0.2 ≤ x ≤ 1.5) and Y₄M₃₋ₓAuₓ₀₊₀ (0.2 ≤ x ≤ 0.4) phases, anisotropic displacement parameters for Gd₄M₃Au₁₀(1)Au₁₀(2,2,1) and Y₄M₃Au₁₀(2,2,1)Au₁₀(2,0,2), and individual interatomic distances and ICOHP values per cell; figures showing observed and simulated powder X-ray diffraction patterns for Gd₄M₃Au₁₀(2,2,1)Au₁₀(2,0,2) and Y₄M₃Au₁₀(2,2,1)Au₁₀(2,0,2) sinusoidal layers in Gd₄M₃Au₁₀Au₁₀(2,3,2) molecular orbital energy diagram for Mn@Au₈ with Mn in $\text{C}_{2h}$ point symmetry, and crystallographic information files of orthorhombic Gd₄M₃Au₁₀(2,0,2) (x ≈ 0.2, 0.25, 0.6, 1.0, 1.5), and Gd₄M₃Au₁₀(2,0,2) (x ≈ 0.2, 0.3, and 0.4). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

Deceased.

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