Hf₃Fe₄Sn₄ and Hf₉Fe_{4- α} Sn_{10+ α} : two stannide intermetallics with low-dimensional iron sublattices

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Abstract

This Article reports two new Hf-rich intermetallics synthesized using Sn flux: Hf₃Fe₄Sn₄ and Hf₉Fe_{4- α} Sn_{10+ α} . Hf₃Fe₄Sn₄ adopts an ordered variant the Hf₃Cu₈ structure type in orthorhombic space group *Pnma* with unit cell edges of $a = 8.1143(5)$ Å, $b = 8.8466(5)$ Å, and $c = 10.6069(6)$ Å. Hf₉Fe_{4- α} Sn_{10+ α} , on the other hand, adopts a new structure type in *Cmc2₁* with unit cell edges of $a = 5.6458(3)$ Å, $b = 35.796(2)$ Å, and $c = 8.88725(9)$ Å for $\alpha = 0$. It exhibits a small amount of phase width in which Sn substitutes on one of the Fe sites. Both structures are fully three-dimensional and are characterized by pseudo one- and two-dimensional networks of Fe – Fe homoatomic bonding. Hf₉Fe_{4- α} Sn_{10+ α} exhibits antiferromagnetic order at $T_N = 46(2)$ K and its electrical transport behavior indicates that it is a normal metal with phonon-dictated resistivity. Hf₃Fe₄Sn₄ is also an antiferromagnet with a rather high ordering temperature of $T_N = 373(5)$ K. Single crystal resistivity measurements indicate that Hf₃Fe₄Sn₄ behaves as a Fermi liquid at low temperatures, indicating strong electron correlation.

Keywords: Flux Synthesis; Intermetallic Compounds; X-ray Crystallography; Magnetism

Introduction

The inability to predict phases with new structures from first principles makes exploratory synthesis an essential feature of materials discovery efforts. This is especially true for intermetallic compounds, where comprehensive electron counting rules that predict material stability are lacking in many, though not all, cases.¹⁻⁴ Our approach to the discovery of new intermetallic compounds focuses on the flux technique in order to promote reactant diffusion to overcome kinetic barriers, allowing discovery and single crystal growth of new phases.^{5,6}

A few compounds have been reported in the Hf – Fe – Sn ternary system. Four of these compounds are structurally related in varying degrees to HfFe₂ Laves phase parent compounds⁷ while a more Hf-rich compound Hf₆Fe_{1.5+x}Sn_{1.5-x} adopts a disordered, ternary variant of the hexagonal Fe₂P structure type.⁸ The four Laves-based Hf – Fe – Sn compounds are all ferromagnets with Curie temperatures ranging from 467(2) K to 658(2) K. All exhibit 2D or 3D homoatomic Fe bonding networks, a common feature in ternary Fe – Sn intermetallics.⁷ However, high temperature ferromagnetism is not a universal feature of ternary iron stannide intermetallics,⁹ and further investigation of the structure and properties of other Hf – Fe – Sn compounds might shed light on this discrepancy. A number of ternary iron stannide intermetallics are known. One major family of these materials is Heusler alloys,¹⁰ which do not have a distinct Fe homoatomic bonding network and whose magnetic order depends on the overall electron count.¹¹ One member of this family, TiFe₂Sn, exhibits a hybridization gap,¹² because it fulfills the exact electron count required to be a semiconducting Heusler alloy. R₆Fe₁₃Sn (R = La, Nd, and Pr) adopt a structure with a complex 2D Fe layer separated by R and Sn atoms interspersed.¹³⁻¹⁵ The Nd and Pr analogues order ferrimagnetically at 374 K and 396 K, respectively, and have been investigated due to their similarity to Nd – Fe – B commercial hard magnets.¹⁶ They undergo spin rearrangements at low temperature, and their magnetic behavior has been primarily attributed to the Fe sublattice.¹⁴ The largest and most diverse family of Fe – Sn ternary intermetallics is the RFe₆Sn₆ compounds, where R represents a rare earth element. The RFe₆Sn₆ structure is based on a Fe – Sn framework with the CoSn structure, and long range order varies significantly depending on the identity of R as different R atoms fill voids in the CoSn framework in many different ways.¹⁷⁻¹⁹ The Fe – Sn network includes slabs of 2D Fe bonding networks incorporated into a fully 3D structure. Magnetic properties of the RFe₆Sn₆ compounds are quite interesting. Typically, the Fe sublattice orders antiferromagnetically between 540 K and 560 K for all cases regardless of the identity of R.²⁰⁻²² For magnetic R atoms, the R

sublattice orders independently at temperatures ranging from roughly 45 K to 3 K and can adopt either a ferromagnetic arrangement or more complicated ordering.^{9,23}

While little is known about the Hf – Fe – Sn phase diagram, the Zr – Fe – Sn phase diagram has been more extensively explored because it is relevant to the design of nuclear reactor shielding and engineering controls.²⁴⁻²⁶ Hf and Zr have nearly identical chemistry in most situations, and as expected $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ adopts the same orthorhombic structure as the $\text{Zr}_3\text{Fe}_4\text{Sn}_4$ analogue, which has been explicitly identified by metallography and powder X-ray diffraction.^{24,26} The structure is an ordered variant of the Hf_3Cu_8 structure type²⁷ in which the Fe and Sn adopt the Cu sites in a perfectly ordered fashion. This structure type can also accommodate other ordered ternary compositions with transition metals and main group elements occupying the Cu sites, the best example of which is $\text{Sc}_3\text{Mn}_2\text{Ga}_6$.²⁸ $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ is most likely also a direct analogue of a reported but uncharacterized Zr compound.²⁵ In this manuscript we report the synthesis, crystal structures, and physical properties of $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ and $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$, two new ternary intermetallic compounds. Both adopt interesting three-dimensional structures with two- and one-dimensional Fe sublattices, respectively. Both compounds are antiferromagnets with $T_N = 46(2)$ K for $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ and $T_N = 373(5)$ K for $\text{Hf}_3\text{Fe}_4\text{Sn}_4$.

Experimental Details

General synthetic details All materials were used as received from their respective suppliers and all handling of air sensitive Hf and Fe powders was done in a nitrogen glove box. Synthetic procedures were very similar to those used in ref. 7. For each reaction Hf powder (Alfa Aesar, 99%, ~325 mesh), Fe powder (Cerac, 99.99%, ~325 mesh), and Sn pieces (American Elements or Sigma Aldrich, 99.999%) were placed in an alumina crucible. The crucible was then placed in a fused silica tube, a stainless steel filter and alumina counterweight was placed atop the crucible and the entire setup was sealed under vacuum ($< 1 \times 10^{-3}$ mbar). The sealed tube was placed in a tube furnace for reaction. The reactions yielding the best products all used essentially the same heating profile: heat to 1100 °C over 17 h followed by cooling over 50 h to 850 °C. After soaking at 850 °C for a few hours the tube was quickly removed from the furnace and centrifuged to remove excess Sn flux. Residual Sn flux was removed from the resulting products in the crucible and stuck to the filter by soaking in dilute HCl. In some reactions a dwell time of 30 min was added at 1100 °C to ensure that the sample successfully reached the target temperature. When present, ferromagnetic materials were removed

from mixtures by bar magnet. Ferromagnetic side products were only observed in product mixtures with a Hf:Fe ratio of near 1:1 and were not present in most reactions.

Synthesis of $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ The best $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ synthesis used 3 equivalents Hf (0.536 g), 4 equivalents Fe (0.223 g), and 30 equivalents Sn flux (3.561 g). After removal of Sn flux, such reactions do not produce any material that is attracted to a bar magnet at room temperature and $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ is the major product. The $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ crystals produced by these reactions are metallic silvery blocks. A typical yield for this reaction is roughly 70%, although a precise yield can be difficult to determine due to the presence of residual Sn flux in some cases. $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ crystals can also be obtained in reasonable yield from a reaction of nearly 1 equivalent Hf (0.375 g), 1 equivalent Fe (0.117 g), and 30 equivalents Sn (7.478 g). These larger reactions with lower Hf and Fe concentrations contain a significant amount of $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$, so determining a precise yield is difficult because of the similar appearance of the crystals.

Synthesis of $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ The best synthesis used 3 equivalents Hf (0.536 g), 1 equivalent Fe (0.056 g), and 30 equivalents Sn flux (3.561 g). After flux removal by etching in HCl, $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ is the major product. Yields relatively low for these reactions, typically in the range of 30 – 40%. Reactions using this reactant ratio always yield products where $x > 0$, and we could not achieve precise control of x with our flux synthesis. $\text{Hf}_9\text{Fe}_4\text{Sn}_{10}$ ($x = 0$) crystals were obtained from syntheses with reactant ratios of 1 Hf (0.375 g) to 1 Fe (0.117 g) to 30 equivalents Sn (7.478 g). Such reactions yield a mixture of products, as mentioned above.

Powder X-ray diffraction Purity and identity of reaction mixtures was assessed with powder X-ray diffraction. Ground samples were mounted on borosilicate glass slides with double-sided tape. Patterns were collected using an Inel CPS120 diffractometer equipped with Cu $K\alpha$ radiation (1.5406 Å) in reflectance geometry.

Single crystal X-ray diffraction Single crystal X-ray diffraction patterns were collected at room temperature on crystals picked from reaction mixtures. Crystals were mounted on glass fibers with glue and diffraction patterns measured using a Stoe IPDS2 or IPDS2T diffractometer equipped with Mo $K\alpha$ radiation (0.71073 Å). Multiple crystals of each compound were screened to confirm identity and crystal quality by collecting a few frames of data. Full sphere diffraction data were collected on the best crystals. The data were indexed, reduced, integrated, and corrected for absorption using the X-Area software suite provided by Stoe.²⁹ The crystal structures were solved and refined using the SHELX suite.³⁰ For all $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ crystals each non-Sn atomic position was independently checked for Sn occupation by allowing the occupancy to freely vary. Only free refinement of the Fe1

site improved the refinement statistics and refined more than 2 standard deviations away from 100% occupancy, indicating some Sn substitution on that site. This Sn substitution is not present in all refinements, suggesting phase width. Most refined $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ crystals were twinned, which was accounted for by using a twin command of -1 0 0 0 1 0 0 0 -1 in each of the refinements.

Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDS) Products were imaged using with a Hitachi S3400N-II scanning electron microscope (SEM) operating with a 20 kV accelerating voltage. Samples were mounted on aluminum stubs with carbon tape. Elemental analysis was performed using energy dispersive X-ray spectroscopy (EDS) with an INCAx-act SDD EDS detector. Spectra were collected on unpolished, clean crystal faces with acquisition times of 60 s. Spectra were collected at multiple locations for each crystal to confirm homogeneity. EDS spectra of $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ correspond to a composition of $\text{Hf}_{3.0(2)}\text{Fe}_{4.0(3)}\text{Sn}_{3.9(1)}$ and spectra collected from $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ yield a composition of $\text{Hf}_{9.0(4)}\text{Fe}_{3.9(3)}\text{Sn}_{11.1(6)}$, both in agreement with the refined compositions from single crystal diffraction to within instrumental error.

Magnetization Measurements Magnetization was measured on collections of crystals crushed to a coarse powder and contained with glue in a gel capsule. The capsules were wrapped in Teflon tape and stuck in a straw. For all measurements presented in this manuscript, each crystal was screened with X-ray diffraction to determine the unit cell and confirm that it was indeed the correct material. Magnetization was measured using a Quantum Design MPMS. To determine the number of moles present in $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10-x}$ samples, the assumption $x = 0$ was used.

Resistivity Measurements Resistivity was measured on twinned or single crystal samples using a Quantum Design PPMS. Contacts were made in a linear 4-probe geometry with copper wire attached to the crystals with silver paste. Screening by single crystal X-ray diffraction confirmed the identity of each measured crystal. Sample dimensions were measured by SEM.

Results and Discussion

Reaction chemistry The title compounds were discovered from Sn flux reactions during attempts to optimize the synthesis of Sn-substituted HfFe_2 Laves phase ferromagnets. The previously reported ferromagnets all form best in Sn flux melts with higher Fe concentration than Hf concentration.⁷ In contrast, $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ tend to form in Sn flux when more Hf is present in the melt than Fe and $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ preferentially forms when larger amounts of both Hf and Fe are dissolved in the flux. In dilute reactions with a Hf:Fe ratio near 1:1, both $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ and $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ are often present

alongside ferromagnetic Laves phases, which are easily separated with a bar magnet. Reactions near this 1:1 ratio are highly sensitive to slight off-stoichiometry in loading. Reactions often contain mixtures of products that vary in relative amount from reaction to reaction. As expected, a higher concentration of Hf in the melt leads to the incorporation of more Hf into the products, stabilizing the title compounds at the expense of the comparatively Hf poor Laves phases. Since these reactions sometimes yield a mixture of $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ and $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$, all crystals used for physical properties measurements were screened by single crystal diffraction to ensure their identity. These reactions do, however, yield relatively large crystals suitable for physical properties measurements (Figure 1).

The very strong chemical similarity of Hf and Zr make Zr – Fe – Sn phase diagrams an attractive comparison point for understanding the behavior of the Hf system. Sections of the ternary phase diagram of Zr – Fe – Sn at both 800 °C²⁵ and 900 °C²⁶ have been reported. $\text{Zr}_3\text{Fe}_4\text{Sn}_4$ is thermodynamically stable at both temperatures, strongly suggesting that $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ is also thermodynamically stable. These phase diagrams also identify a phase with composition $\text{Zr}_{9.0(5)}\text{Fe}_{3.8(1)}\text{Sn}_{9.5(5)}$ that the authors term the *X* phase.²⁵ It exhibits a slight phase width based on elemental analysis and crystallographic parameters were not determined. This phase is also thermodynamically stable at both 800 °C and 900 °C, immediately above and below the temperature at which we isolated $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$. The composition, phase width, and chemical similarity between Hf and Zr strongly suggest that the *X* phase reported previously is in fact $\text{Zr}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$. This would indicate that $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$, like $\text{Hf}_3\text{Fe}_4\text{Sn}_4$, is most likely thermodynamically stable as well.

Hf₃Fe₄Sn₄ Structure $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ adopts a fully ordered variant of the Hf_3Cu_8 structure type in which the Fe and Sn occupy the Cu sites. Refinement details and atomic positions can be found in Tables 1 and 2, respectively, and the structure is shown in Figure 2. It crystallizes in the orthorhombic space group *Pnma* with unit cell parameters of $a = 8.1143(5)$ Å, $b = 8.8466(5)$ Å, and $c = 10.6069(6)$ Å. The compound, which is isostructural to the Zr analogue, contains two crystallographically distinct Hf positions, three distinct Sn positions and three distinct Fe positions. It is a fully three-dimensional structure best understood when viewed as made up of two main components: a pseudo two-dimensional Fe sublattice and Hf atoms coordinated by Sn linking the Fe layers.

The Fe sublattice consists of two-dimensional networks of corrugated 10-membered Fe rings in the *bc* plane, highlighted in Figure 3c. The rings are composed exclusively of Fe-Fe bonds that range from 2.610 to 2.760 Å. This layer extends infinitely in two dimensions and is significantly corrugated, occupying a width of roughly 1.98 Å along the *a* axis. The Fe layers are $\frac{1}{2} * a$ (4.06 Å) apart from one another at their closest point along the *a* axis, and are bridged by bonds to single Sn

and Hf atoms. Sn and Hf atoms also fill the voids left by the middle of the 10-membered rings. Most of the Fe atoms are bonded only to Sn atoms in addition to their Fe-Fe bonds with interatomic distances between 2.53 to 2.90 Å. Fe7 is the only exception and bonds to both Hf1 and Hf2 with bond lengths of 2.911 and 2.943 Å, respectively, in addition to its Fe-Sn bonds.

The Hf1 atom is situated on Wyckoff position $8d$ and forms a dimer with a symmetry equivalent atom with an Hf – Hf bond length of 3.098 Å. This dimer, shown in Figure 3b, directly bridges the Fe layers by bonding to Fe7 atoms in two adjacent layers. The remainder of the coordination sphere of each atom of the Hf – Hf dimer is composed of a highly distorted Sn octahedron. Hf2 sits on the $4c$ Wyckoff site is coordinated by 9 atoms, 7 Sn atoms and two Fe atoms (Figure 3a). The Sn atoms form a distorted pentagonal bipyramid. In contrast to Hf1, Hf2 does not bridge between Fe pseudolayers and instead partially fills the void in the middle of the Fe rings. Two of the Sn atoms bridge the Fe pseudolayers and are coordinated to the Hf1 dimer. The remaining Sn atom occupies the middle of the void in the Fe ring and is bonded to Hf2.

Hf₉Fe_{4- x} Sn_{10+ x} Structure Hf₉Fe_{4- x} Sn_{10+ x} crystallizes in the orthorhombic $Cmc2_1$ space group in a new structure type, shown in Figure 4. While it does exist as an exactly stoichiometric compound, it also exhibits a small degree of phase width in which excess Sn substitutes onto one of the Fe sites. The ideal composition yields unit cell parameters of $a = 5.6458(3)$ Å, $b = 35.796(2)$ Å, and $c = 8.88725(9)$ Å with a volume of 1791.1(2) Å³. Sn substitution leads to an increase in the unit cell parameters as Sn is larger than Fe. In addition to the parent $x = 0$ compound, we also present a structure solution from single crystal diffraction on a crystal where $x = 0.32$ based on refined Sn/Fe occupancy, which yields a unit cell of $a = 5.6777(4)$ Å, $b = 35.875(2)$ Å, $c = 8.8725(9)$ Å with a volume of 1807.2(3) Å³, about 0.9% larger than the unit cell for the stoichiometric composition. Refinement details for both solutions can be found in Table 1 and atomic coordinates in Table 3. The Sn substitution shows a strong preference for the Fe1 site, and does not substitute on the Fe2 site. In addition to the observed electron density, this site preference is illustrated by the fact that the Fe2 – Fe2 bond actually shrinks in the $x = 0.32$ compound (relative to the stoichiometric structure) while the Fe1 – Fe1 bonds lengthen due to the partial substitution of the larger Sn atom. We found no evidence of long range ordering of the Sn substitution. The unit cell is best understood as a series of two chains of Fe – Fe bonds with Sn and Hf atoms surrounding them as ligands separated by regions of Hf – Sn regions.

The two Fe atomic positions are shown in Figure 5d and 5e. In both cases they form Fe – Fe bonds with adjacent Fe atoms parallel to the a axis. In the case of Fe1, which is a mixed Fe/Sn

position when $x > 0$, it forms a 1-dimensional chain of Fe atoms in an alternating arrangement with a longer bond of 2.891(4) Å followed by a shorter bond of 2.755(4) Å in the $x = 0$ case, with both bonds slightly lengthened by Sn substitution. In addition to the long and short Fe chain bonds, the Fe1 atom is also coordinated by a heavily distorted octahedron of Sn atoms that is capped on two faces with Hf atoms also bound to the Fe/Sn atom. The Fe2 position also exhibits Fe – Fe bonding along the a axis, but the Fe atom pairing in this case is much stronger and causes the formation of 2.497(4) Å Fe – Fe dimers separated by > 3.2 Å, too long to be a genuine Fe – Fe bond. Fe2 is also bonded to a 5 Sn atoms and 3 Hf atoms in an irregular 8-vertex polyhedron that shares faces with the neighboring polyhedron around the two adjacent Fe2 positions, both the one it is bound to as part of a dimer as well as the more distant unbound one. The ligand Sn and Hf atoms are shared between these two Fe chains or dimers, making up a slab of the structure that is primarily Sn and Fe atoms. These slabs are interspersed along the b axis with Sn – Hf regions, highlighted in Figure 3a and 3b. The segregation of primarily Hf – Sn regions from any Fe atoms is a phenomenon also observed in the modulated $\text{Hf}_{1.82}\text{Fe}_5\text{Sn}_{3.81}$ compound,⁷ and may play a role in stabilizing these structures.

Hf atomic environments are shown in Figure 5a – 5c. Three crystallographically distinct Hf atoms sit in very similar environments at the center of heavily distorted pentagonal bipyramids composed of 7 Sn atoms. The final Hf atom that is not described by bonding to the Fe chain and dimer is Hf5, shown in Figure 5c. It is surrounded by 8 atoms: a heavily distorted Sn octahedron, and two Hf atoms with a bond angle of 180 degrees, forming a linear Hf chain parallel to the a axis, similar to the Fe chains. The bonds in this chain of Hf atoms also alternate in a long – short – long – short fashion, but the long bonds are only about 0.03 Å longer than the short ones, a much smaller difference than in the case of the Fe chains. In addition to the isolated Hf chain, two of the Hf atoms that coordinate to the Fe chain and dimer form a Hf – Hf bond. The local coordination around this Hf – Hf dimer, shown in Figure 5b, is quite similar to the atomic arrangement around the Hf – Hf bond in $\text{Hf}_3\text{Fe}_4\text{Sn}_4$. In both cases, two Fe and two Sn atoms surround the bond equidistant from the two Hf atoms. Hf1 is coordinated by 4 additional Sn atoms in a configuration very similar to the coordination in $\text{Hf}_3\text{Fe}_4\text{Sn}_4$. Hf7 is also coordinated by 4 additional Sn atoms and as well as the Fe – Fe dimer, which distorts the arrangement of the 4 Sn atoms relative to how they are arranged in $\text{Hf}_3\text{Fe}_4\text{Sn}_4$.

Magnetic Properties Neither of the title compounds are attracted to a bar magnet at room temperature. Figure 6 shows temperature-dependent magnetization measurements for both

$\text{Hf}_3\text{Fe}_4\text{Sn}_4$ and $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$. Magnetization of $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ (Figure 6a) shows clear signs of antiferromagnetic (AFM) order at $T_N = 373(5)$ K. We attribute this relatively high ordering temperature to local magnetic moments on the Fe atoms. Below T_N the magnetization gradually rises as temperature decreases. This is rather unusual for an antiferromagnet, as magnetization would normally approach 0 as temperature approaches 0 K. The origin of this unusual behavior is not clear, and small impurity phases below the detection limit of X-ray diffraction cannot be ruled out. Magnetic order above room temperature is a common feature of iron stannide intermetallics. The 2D Fe sublattice of $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ behaves similarly to the 2D iron sublattice in the RFe_6Sn_6 compounds, exhibiting strong antiferromagnetic coupling between Fe moments that leads to AFM order above room temperature. We were unable to determine the magnitude of the magnetic moment for this compound as our measurements could not reach high enough temperatures for the paramagnetic state to obey a Curie-Weiss law.

Magnetization measurements for $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ is shown in Figure 6b. $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ also exhibits AFM order with $T_N = 46(2)$ K. Since precise determination of x is difficult for these bulk samples, we assumed $x = 0$ in order to convert samples mass to moles. Figure 6b shows a representative measurement, though T_N varied in some samples, indicating that x affects magnetic coupling strength. All observed T_N values were within about 5 K of the measurement we present here. Magnetization below T_N rises as the compound approaches 0 K, slightly unexpected behavior similar to what is observed in $\text{Hf}_3\text{Fe}_4\text{Sn}_4$. Above T_N between 100 and 300 K $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ follows Curie-Weiss behavior with a Weiss constant $\Theta = -22(1)$ K and a Curie constant $C = 9.66(8)$ emu mol⁻¹ Oe⁻¹ K⁻¹, corresponding to an effective magnetic moment $\mu_{\text{eff}} = 2.20(2)$ μ_B/Fe . The Weiss constant indicates moderate antiferromagnetic coupling between Fe moments, consistent with AFM order at 46(2) K. The magnetic moment per Fe atom is slightly larger than the 1-2 μ_B/Fe observed in the Laves phase ferromagnets⁷ and comparable to values reported for RFe_6Sn_6 antiferromagnets.^{22,31} The 1D Fe sublattice in $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ orders at lower temperature than 2D ones in $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ and the RFe_6Sn_6 compounds. The lower ordering temperature is most likely a consequence of weaker coupling brought about by a lower dimensionality Fe network. The Sn substitution on Fe sites could also affect magnetic coupling strength, although predicting exactly how it will do so is difficult as varying x influences competing magnetic effects.

Resistivity Both title compounds exhibit metallic resistivity, as expected. Resistivity values measured as a function of temperature are shown in Figure 7. All three measurements include a small drop in resistivity at ~ 3.7 K due to the superconducting transition of a small amount of Sn

flux (likely less than 2% based on the magnitude of the drop) that could not be removed from the measured crystals. This feature varies in magnitude from crystal to crystal because the amount of residual Sn also varies. Apart from this one common feature, the resistivity for $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ qualitatively differs from that of $\text{Hf}_9\text{Fe}_4\text{Sn}_{10}$ and $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$. $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ exhibits significantly lower resistivity than $\text{Hf}_9\text{Fe}_4\text{Sn}_{10}$ and $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$, probably due to the smaller unit cell. The residual resistivity ratio (RRR, $\rho_{300\text{K}}/\rho_0$) for $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ is 3.4, twice as large as the RRR of both $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ samples, indicating that the $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ sample has higher crystal quality with fewer defects. At low temperatures, $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ deviates from behavior dominated by electron-phonon scattering typical of normal metals. It exhibits a Fermi Liquid state below 30 K modeled by equation 1:

$$\rho(T) = \rho_0 + \beta T^2$$

where ρ_0 represents residual resistivity and β is a scale factor. For the $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ sample presented here, $\rho_0 = 50.39(7) \mu\Omega \text{ cm}$ and $\beta = 1.92 \times 10^{-2} \mu\Omega \text{ cm K}^{-2}$. The T^2 dependence of the resistivity indicates that electron-electron scattering dominates the resistivity in this temperature range. Such correlated electron behavior is most likely related to the strong magnetic coupling between the Fe atoms that causes high temperature magnetic order.

$\text{Hf}_9\text{Fe}_4\text{Sn}_{10}$ and $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ on the other hand obey the Bloch – Grüneisen – Mott (BGM) model for resistivity in metals (equation 2):³²

$$\rho(T) = \rho_0 + AT \left(\frac{T}{\Theta_D} \right)^4 \int_0^{\frac{T}{\Theta_D}} \frac{x^4 dx}{(e^x - 1)(1 - e^{-x})} + KT^3$$

In this model ρ_0 again represents residual resistivity, Θ_D represents the Debye temperature, x represents phonon energies, and A and K are scale factors. Fit details are given in Table 4. The T^5 integral term accounts for electron-phonon scattering, and makes the dominant contribution to the resistivity of $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ for both measured x values. The T^3 term describes interband scattering at the Fermi level³³ and makes a much smaller contribution. The significant difference in Θ_D between the two samples is due to experimental factors, not intrinsic behavior. While the Debye temperature for $x = 0$ is most likely slightly higher than for $x > 0$, a difference this large is most likely because

resistivity measurements are a relatively indirect probe of Θ_D and consequently easily biased by experimental conditions. In spite of the discrepancy in Θ_D , the overall phonon-dominated behavior of the two samples is quite similar. This behavior indicates that unlike in the case of $\text{Hf}_3\text{Fe}_4\text{Sn}_4$, $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ behaves as a normal metal and does not show any signs of strong electron correlation.

Conclusion

$\text{Hf}_3\text{Fe}_4\text{Sn}_4$ and $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ are new intermetallic compounds that can be prepared with a reactive Sn flux technique. They adopt complex and interesting structures with 2- and 1-dimensional Fe bonding networks, respectively. Both adopt structures to analogous Zr compounds and are most likely thermodynamically stable. $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ is an antiferromagnet with a Neel temperature of 46(2) K and $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ orders antiferromagnetically at $T_N = 373(5)$ K. For both $x = 0$ and $x > 0$, $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ exhibits normal metallic resistivity that is relatively high, most likely due to its large and complex unit cell. $\text{Hf}_3\text{Fe}_4\text{Sn}_4$ exhibits Fermi liquid behavior at low temperature due to electron correlations arising from antiferromagnetic coupling.

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Tables

Table 1. Single Crystal X-ray refinement details for the title compounds

Empirical formula, Z	Hf ₉ Fe _{3.67} Sn _{10.33} , 4	Hf ₉ Fe ₄ Sn ₁₀ , 4	Hf ₃ Fe ₄ Sn ₄ , 4
Formula weight (g/mol)	3037.63	3016.89	1233.63
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	<i>Cmc</i> 2 ₁	<i>Cmc</i> 2 ₁	<i>Pnma</i>
Unit cell dimensions (Å)	<i>a</i> = 5.6778(11) <i>b</i> = 35.876(7) <i>c</i> = 8.8727(18)	<i>a</i> = 5.6458(3) <i>b</i> = 35.797(2) <i>c</i> = 8.8628(6)	<i>a</i> = 8.1143(16) <i>b</i> = 8.8466(18) <i>c</i> = 10.607(2)
Volume (Å ³)	1807.3(6)	1791.18(18)	761.4(3)
Density (calc, g/cm ³)	11.088	11.187	10.762
Abs coefficient (mm ⁻¹)	67.92	68.616	60.835
F(000)	5008	5008	2080
Crystal size (μm)	100 × 80 × 20	267 × 250 × 13	90 × 40 × 10
θ range (deg)	2.27 to 29.16	2.28 to 29.17	3.84 to 38.00
Index ranges	-7 ≤ <i>b</i> ≤ 7, -48 ≤ <i>k</i> ≤ 48, -12 ≤ <i>l</i> ≤ 12	-7 ≤ <i>b</i> ≤ 7, -48 ≤ <i>k</i> ≤ 48, -12 ≤ <i>l</i> ≤ 12	-13 ≤ <i>b</i> ≤ 13, -13 ≤ <i>k</i> ≤ 15, -18 ≤ <i>l</i> ≤ 18
Reflections collected	8841	8722	13187
Independent reflections	2659 [R _{int} = 0.0628]	2649 [R _{int} = 0.0497]	2138 [R _{int} = 0.0978]
Completeness	99.6%	99.5%	98.7%
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	2659 / 1 / 131	2649 / 1 / 129	2138 / 0 / 59
Goodness-of-fit	1.082	1.091	1.071
Final R indices [>2 σ (I)]	R _{obs} = 0.0289, wR _{obs} = 0.0702	R _{obs} = 0.0300, wR _{obs} = 0.0725	R _{obs} = 0.0476, wR _{obs} = 0.1033
R indices [all data]	R _{all} = 0.0300, wR _{all} = 0.0706	R _{all} = 0.0313, wR _{all} = 0.0730	R _{all} = 0.0625, wR _{all} = 0.1085
Extinction coefficient	0.000267(15)	0.000108(12)	0.00317(19)
diff. peak and hole (e·Å ⁻³)	2.922 and -3.617	4.557 and -4.334	4.668 and -5.643

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR = (\sum [w(|F_o|^2 - |F_c|^2)^2] / \sum [w(|F_o|^4)])^{1/2}$ and calc $w = 1/[\sigma^2(F_o^2) + (w1 \cdot P)^2 + w2 \cdot P]$ where $P = (F_o^2 + 2F_c^2)/3$ where w1 and w2 are refined weights.

Table 2. Fractional atomic coordinates and displacement parameters for Hf₃Fe₄Sn₄

Label	x	y	z	Occupancy	$U_{eq}^a (\text{\AA}^2 \times 10^3)$
Hf(1)	0.4502(1)	0.0512(1)	0.3656(1)	1	7(1)
Hf(2)	0.0498(1)	1/4	0.4455(1)	1	8(1)
Sn(3)	0.7391(2)	1/4	0.2867(1)	1	5(1)
Sn(4)	0.3823(1)	0.4308(1)	0.3548(1)	1	7(1)
Sn(5)	0.3814(2)	1/4	0.5804(1)	1	6(1)
Fe(6)	0.6839(3)	1/4	0.5216(2)	1	7(1)
Fe(7)	0.2997(2)	0.5072(2)	0.4038(2)	1	9(1)
Fe(8)	0.1278(3)	1/4	0.2361(2)	1	6(1)

^a defined as one third of the orthogonalized U_{ij} tensor.

Table 3. Fractional atomic coordinates and displacement parameters for $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$

Label	x	y	z	Occupancy	$U_{eq}^a (\text{\AA}^2 \times 10^3)$
Hf(1)	0.2514(1)	0.0301(1)	0.3336(1)	1	5(1)
Hf(2)	0	0.0515(1)	0.7256(1)	1	6(1)
Hf(3)	0	0.0961(1)	0.1188(1)	1	4(1)
Hf(4)	0	0.1688(1)	0.6015(1)	1	6(1)
Hf(5)	0	0.1772(1)	0.0400(1)	1	5(1)
Hf(6)	0	0.3004(1)	0.3153(1)	1	7(1)
Hf(7)	0	0.3960(1)	0.0583(1)	1	6(1)
Hf(8)	0	0.4509(1)	0.4551(1)	1	6(1)
Sn(1)	0.2462(2)	0.3780(1)	0.3472(2)	1	4(1)
Sn(2)	0	0.0193(1)	0.0384 (2)	1	3(1)
Sn(3)	0	0.0952(1)	0.4534(2)	1	4(1)
Sn(4)	0	0.2185(1)	0.3251(2)	1	7(1)
Sn(5)	0	0.3144(1)	0.2695(2)	1	6(1)
Sn(6)	0	0.4758(1)	0.1352(2)	1	4(1)
Sn(7)	0	0.5964(1)	0.2189(2)	1	4(1)
Sn(8)	0	0.6868(1)	0.1309(2)	1	8(1)
Sn(9)	0	0.7675(1)	0.3094(2)	1	7(1)
Fe/Sn(1)	0.2442(3)	0.2512(1)	0.0649(2)	0.83/0.17(1)	8(1)
Fe(2)	0.2180(3)	0.1502(1)	0.3133(2)	1	6(1)

^a defined as one third of the orthogonalized U_{ij} tensor.

Table 4. BGM fit parameters and residual resistivity ratio for $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$ single crystals

Formula	ρ_0 ($\mu\Omega$ cm)	A ($\mu\Omega$ cm K ⁻¹)	Θ_D (K)	K ($\mu\Omega$ cm K ⁻³)	RRR
Hf ₉ Fe ₄ Sn ₁₀	401.8(1)	1.045(1)	131.1(1)	$1.05(1) \times 10^{-6}$	1.7
Hf ₉ Fe _{4-x} Sn _{10+x}	809.3(5)	2.445(5)	87.9(1)	$5.26(6) \times 10^{-6}$	1.7

Figures

Figure 1 SEM images of both (a) Hf₃Fe₄Sn₄ and (b) Hf₉Fe_{4-x}Sn_{10+x}. Pits on the crystal surfaces are a result of HCl over-etching to remove excess Sn flux.

Figure 2 Crystal structure of $\text{Hf}_3\text{Fe}_4\text{Sn}_4$. (a) Projection down the a axis with the topmost 2D Fe net as well as Sn and Hf atoms between the two nets in a single unit cell highlighted. (b) Projection down the b axis with only Hf – Hf and Fe – Fe bonds shown. (c) Projection down the c axis, again with only Hf – Hf and Fe – Fe bonds shown. All other bonds are omitted for clarity. (d) The structure viewed down the b axis with the 2D corrugated Fe network, Hf – Hf bonds, and HfSn_7 polyhedra highlighted.

Figure 3 Local coordination in $\text{Hf}_3\text{Fe}_4\text{Sn}_4$. (a) HfSn_7 polyhedron including two capping Fe atoms bonded to the central Hf atom. (b) Local coordination around the Hf – Hf dimer. (c) A single Fe network layer viewed down the a axis. The 10 membered rings are clearly visible from this angle.

Figure 4 $\text{Hf}_7\text{Fe}_{4-x}\text{Sn}_{10+x}$ structure. (a) View down the a axis, with the Fe – Sn regions highlighted in orange. The circled Hf atoms indicate the location of Hf chains that extend along the a axis (coming out of the page in this panel). Only homoatomic Hf – Hf and Fe – Fe bonds are shown for clarity. (b) View down the c axis, again with only Hf – Hf and Fe – Fe bonds shown for clarity. The Fe/Sn chains and Fe dimers are visible, as is the distinct Hf – Sn region near the center of the unit cell. (c) Structure viewed down the a axis with distorted HfSn_7 polyhedra drawn in blue.

Figure 5 Local coordination environments in $\text{Hf}_9\text{Fe}_{4-x}\text{Sn}_{10+x}$. (a) distorted HfSn_7 pentagonal bipyramid. Three other crystallographically distinct bipyramids are also present in the structure with slightly different distortions and are not shown here. (b) Hf – Hf dimer and surrounding coordination. (c) Hf chain that extends along the a axis. (d) and (e) show the local coordination around the long – short alternating bond length Fe/Sn chain and Fe – Fe dimer, respectively.

Figure 6 Magnetization as a function of temperature for (a) $\text{Hf}_9\text{Fe}_4\text{Sn}_{10}$ and (b) $\text{Hf}_3\text{Fe}_4\text{Sn}_4$. Note the different temperature range of the two measurements, as well as the differing y axis scales. The two insets show a more detail at the transition temperatures for each compound.

Figure 7 Resistivity as a function of temperature for the title compounds. (a) All three compounds and associated fits to the measured data. The Sn occupancy of the unsubstituted $\text{Hf}_9\text{Fe}_4\text{Sn}_{10}$ sample was confirmed by single crystal diffraction. The small drop seen in each compound at low temperature corresponds to the superconducting transition of residual Sn flux. (b)

A comparison of the Fermi Liquid model and BGM model to low temperature data for $\text{Hf}_9\text{Fe}_4\text{Sn}_{10}$, highlighting that BGM is a much better model for this compound. The $x > 0$ analogue is not shown, but is quite similar. (c) A comparison of the Fermi liquid and BGM models for $\text{Hf}_3\text{Fe}_4\text{Sn}_4$. The Fermi liquid model is clearly a better fit to the data.