Supplementary information

Coherent Magnetic Nanoinclusions Induce Charge Localization in Half-Heusler Alloys Leading to High-*T*c Ferromagnetism and Enhanced Thermoelectric Performance

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Result and Discussion

Structure and Composition. All major diffraction peaks on the XRD patterns of various compositions can be indexed to the cubic MgAgAs structure (Figure S1). However, a close-up look at the 220 peak indicated splitting, suggesting the presence of multiple phases with closely related crystal structure and similar lattice parameters. For the samples with x = 0 and x = 0.02, three shoulder peaks can be identified that are associated with the formation of Ti-rich and Zr-rich phases embedded within an Hf-rich HH matrix (Figure S2b). The PXRD analysis is also consistent with the back-scattered electron (BSE) images of these two samples (Figure S3), which show a random dispersion of the Ti-rich HH domains (black) within a (Zr, Hf)-rich (grey) HH matrix. Upon increasing the Fe content to 5 at%, the shoulder peaks disappear leading to a large single 220 peak. This suggests either a decrease in the fraction of the Ti-rich phase within the (Zr/Hf)-rich HH matrix, or the formation of the Ti-rich phase with very small sizes and/or the coexistence of multiple phases with very similar lattice parameters. Indeed, the SEM images of the sample with x = 0.05 revealed the presence of a small fraction of microscale Ti-rich phase (Figure 1 and S3), and HRTEM images of the (Zr,Hf)-rich regions indicate the formation of nanometer scale Tirich inclusions. In addition, composition mapping and EPMA (electron probe microanalysis) point analysis (Table S1) revealed the coexistence in various Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_x)Sn_{0.975}Sb_{0.025} compositions of a Ti-rich FH phase with composition Ti(Ni_{4/3}Fe_{2/3})Sn along with Zr-rich and Hf-rich HH phases. It is interesting to note from the EPMA result (Table S1) that while the Ti_{0.25}Zr_{0.25}Hf_{0.5}NiSn_{0.975}Sb_{0.025} HH composition naturally phase separates into Ti-rich and (Zr,Hf)-rich phases, the added Fe tends to mix exclusively with the Ti phase to form (Ti,Fe)-rich nanoinclusions (Ti($Ni_{4/3}Fe_{2/3}$)Sn) with the FH structure embedded within the (Zr,Hf)-rich HH matrix. The lattice parameter of the Ti(Ni_{4/3}Fe_{2/3})Sn phase in the cubic FH structure (Fm-3m) was estimated to be 6.073 Å assuming the formation of a TiNi_{2-v}Fe_vSn solid solution (with y = 2/3) between TiNi₂Sn (a = 6.076 Å).¹ and TiFe₂Sn.(a = 6.068 Å).^{2,3} The similarity in the lattice parameters of the Ti(Ni_{4/3}Fe_{2/3})Sn FH phase and the solid solutions between the HH phases (F-43m) TiNiSn (a = 5.930 Å),¹ ZrNiSn (a = 6.123 Å),⁴ and HfNiSn (a = 6.0756 Å),⁵ helps explain the overlapping of their 220 peaks in the sample with x = 0.05 (Figure S1). As the Fe content in the starting mixture increases, the population density and average size of the (Ti,Fe)-rich FH phase, Ti(Ni_{4/3}Fe_{2/3})Sn, within the resulting composites increase (Figure S3 and Table S1-S2) whereas the fraction of Ti within the matrix decreases according to the chemical equation (1).

 $\begin{array}{l} 0.25 \ Ti + 0.25 \ Zr + 0.5 \ Hf + Ni + Sn + x \ Fe \rightarrow 3x/2 \ Ti(Ni_{4/3}Fe_{2/3})Sn \ (FH \ inclusion) + [Ti_{(0.25-1.5x)}Zr_{0.25} \ Hf_{0.5}]Ni_{(1-2x)}Sn_{(1-1.5x)} \ (HH \ matrix) \ (1) \end{array}$

Therefore, as the Fe content increases, an increasingly larger fraction of the sample consists of the $Ti(Ni_{4/3}Fe_{2/3})Sn$ FH phase and Hf-rich HH phase with a smaller lattice parameter (6.073 Å) compared to ZrNiSn (6.123 Å). Accordingly, the magnitude of the 220 high angle shoulder peak increases for the

samples with x = 0.1 and 0.15 (Figure S1), whereas the intensity of the low angle shoulder peak attributed to the Zr-rich HH phase remains essentially unchanged.

The proposed chemical equation is consistent with elemental mapping showing the distribution of various elements within the composites (**Figure S4**). It can be seen that the added elemental Fe preferentially incorporates into the Ti-rich phase (**Figure S4**) to form the Ti(Ni_{4/3}Fe_{2/3})Sn phase. The chemical composition of the FH inclusion phase was confirmed by EPMA point analysis result (**Table S1**), and the FH atomic structure of the Ti(Ni_{4/3}Fe_{2/3})Sn inclusion phase was confirmed by the atomic resolution transmission electron microscopy image on the samples with x = 0.05 (**Figure 1d**).

The effect of Fe incorporation on the redistribution of elements amongst various phases coexisting within the composite was carefully investigated through a combination of energy dispersive spectroscopy (EDS), EPMA point analysis and SEM. For instance, composition mapping images for the $Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_{0.15})Sn_{0.975}Sb_{0.025}$ sample using the EDS spectrum shown in **Figure S4d** clearly reveal the segregation of Ti-rich and Zr-rich phases within the Hf-rich matrix, which is consistent with PXRD results. It is interesting to note the striking similarity in the distribution of Fe and Ti elements within the sample, which confirms that Fe preferentially reacts with Ti to form a (Ti,Fe)-rich phase according to the proposed chemical reaction (1) with the remaining elemental Ti dissolved into the Hf-rich matrix. Additionally, the (Ti,Fe)-rich phase also contains a slightly higher concentration of Ni compared to the Hf-rich matrix. The remaining elements (Sn and Sb) are homogeneously distributed within the sample. Similar redistributions of elements were found in other compositions (**Figures S4a** to **S4d**).

To further probe the effect of Fe incorporation on the microstructure of various composites, backscattered electron (BSE) images were collected on several compositions (Figure S3). As observed from the XRD data, the Fe-free sample segregates into three main phases that are Ti-rich. Zr-rich and Hf-rich (Figure S2), which also appear on the BSE as the dark, grey and bright domains, respectively. Interestingly, the addition of 5 mol% Fe in the starting mixture favors the nucleation of small (Ti,Fe)-rich nanoinclusions (dark contrast) that are widely dispersed within the HH matrix with the largest fraction of Ti atoms integrated into the Zr/Hf-rich HH matrix (Figure 1b and Figure S3). This gives the impression of a large reduction in the overall mole fraction of the Ti-rich phase when compared to the pristine Fe-free sample (Table S2). Upon increasing the Fe content to 10 mol%, the mole fraction of the (Ti,Fe)-rich phase increases, and the fraction of Ti atoms dissolved into the Zr/Hf-rich HH matrix decreases. At this composition, the fraction of Ti available for integration into the ZrHf-rich matrix is 10%, which is within the solubility limit of Ti in HfNiSn or ZrNiSn. Therefore, the microstructure for the sample with 10 mol% Fe as well as that of the sample with 15 mol% Fe only show two main domains, which correspond to the (Ti,Fe)-rich phase (dark) and (Zr,Hf)-rich phase (grey). The sample with 15 mol% Fe displays the largest concentration of the (Ti,Fe)-rich phase (dark), and the (Zr,Hf)-rich HH matrix is nearly Ti-free (Table S1). These observations are consistent with the chemical reaction (1), which predicts that the addition of 16 mol% Fe in the starting mixture should result in the consumption of all Ti atoms leading to the formation of (Ti,Fe)-rich inclusions within a Ti-free (Zr,Hf)-rich HH matrix. The mole fraction of the (Ti,Fe)-rich phase (v_{obs}) formed in the synthesized samples was quantified using Image-J software by extracting the total surface area covered by the (Ti,Fe)-rich domain, which was then divided by the total surface area of the SEM images (Figure S3). The result is compared in Table S2 with the mole fraction (v_{calc}) of the (Ti,Fe)-rich phase anticipated from the chemical equation (1). In general, the calculated mole fraction of the (Ti,Fe)-rich phase extracted from the BSE images increases with the Fe content. However, the observed mole fraction of the (Ti,Fe)-rich phase in all samples remains lower than the anticipated value because the image analysis method used to quantify the density of (Ti,Fe)-rich inclusions is not able to account for submicron scale (Ti, Fe)-rich inclusions that formed during the solid-state reaction of the elements. Remarkably, the discrepancy between the observed (v_{obs}) and the predicted (v_{calc}) mole fraction of the (Ti,Fe)-rich phase drastically decreases with the increasing Fe content, suggesting that as the nominal Fe content increases, the population density of (Ti,Fe)-rich nanoinclusions within the sample rises, leading to agglomeration into larger particles. The discrepancy can be used as an indirect measurement of the mole fraction of subnanometer scale (Ti,Fe)-rich phases within various samples. Within this picture, one can consider that ~78% of the (Ti,Fe)-rich phases formed in the sample with x = 0.05 are at the subnanometer scale (**Table S2**), whereas for the sample with x = 0.15 this number is only ~16%.

To further support the above analysis as well as the reaction mechanism proposed in chemical equation (1), we have obtained accurate chemical composition data for the (Ti,Fe)-rich inclusions and the (Zr,Hf)rich matrix in selected Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_x)Sn_{0.975}Sb_{0.025} samples using multiple points analysis by EPMA. Results are presented in Table S1. For the sample containing 5 at% Fe (x = 0.05), the average composition of the (Ti,Fe)-rich domain (dark contrast) measured from five different points was found to be 23 at% Ti, 32 at% Ni, 17 at% Fe and 26 at% Sn, which is consistent with the chemical composition of a FH phase, $TiNi_{4/3}Fe_{2/3}Sn$, as suggested in the chemical equation (1). The FH structure of the (Ti, Fe)rich phase was also confirmed by the atomic resolution transmission electron microscopy. As shown in Figure 1d and 1e, there is a striking similarity in the ordering of atoms within the (110) crystal planes in the (Ti,Fe)-rich phase (Figure 1d) and the schematic diagram of the (110) plane in the FH structure (Figure 1e). Equivalent planes within the HH structure shows a clearly different atomic packing structure. Interestingly, EPMA data also revealed only a trace amount of Zr (1 at%) and Hf (1.6 at%) within the (Ti,Fe)-rich phase for the sample with x = 0.05. The remaining Ti atoms are mixed with Zr and Hf in the grey phase, with the average composition 7 at% Ti, 15 at% Zr and, 12 at% Hf, 32 at% Ni, 32 at% Sn and 0.4 at% Fe, corresponding to a HH phase with chemical formula Ti_{0.22}Zr_{0.47}Hf_{0.375}NiSn. The bright phase consists exclusively of Hf (34%), Ni (33%) and Sn (32%), which corresponds to the HH phase HfNiSn. Similar analysis of the (Ti,Fe)-rich phase in the sample with 15 at% Fe showed the average composition Ti/Ni/Fe/Sn in the ratio 21.5/31.2/18/26, which can also be approximated to the FH composition TiNi_{4/3}Fe_{2/3}Sn. The HH matrix in the 15 at% Fe sample is composed essentially of a mixture of a Zr-rich phase with composition Zr (29 at%), Ni (33 at%), and Sn (32 at%); and a Hf-rich phase with composition Hf (26 at%), Ni (33 at%), and Sn (32 at%).

Sample Name*	Ti	Zr	Hf	Ni	Sn	Fe	Sb	Ti+Zr+Hf	Ni+Fe	Sn
Fe05_Dark	22.73	1.21	1.53	33.43	26.10	14.92	0.09	25.46	48.35	26.10
Fe05_Dark	22.65	0.77	1.67	29.88	26.06	18.81	0.17	25.09	48.68	26.06
Fe05_Dark	22.61	1.35	1.67	36.30	25.47	12.55	0.04	25.64	48.85	25.47
Fe05_Dark	21.94	0.62	1.92	26.11	25.94	23.29	0.18	24.48	49.40	25.94
Fe05_Dark	23.05	1.32	1.05	35.19	26.55	12.75	0.08	25.42	47.94	26.55
Fe05_Grey	5.07	19.31	8.15	33.67	32.73	0.13	0.95	32.53	33.79	32.73
Fe05_Grey	5.52	24.83	6.23	31.80	30.12	0.49	1.01	36.57	32.29	30.12
Fe05_Grey	11.19	6.23	15.23	32.89	32.50	0.84	1.12	32.66	33.73	32.50
Fe05_Grey	8.05	14.57	14.86	30.01	31.19	0.34	0.98	37.49	30.35	31.19
Fe05_Grey	7.78	9.76	16.06	32.68	32.26	0.35	1.10	33.60	33.03	32.26
Fe05_Light	2.12	1.90	29.86	33.29	32.46	0.06	0.31	33.88	33.36	32.46
Fe05_Light	0.37	0.55	46.56	44.89	0.27	7.39	BDL	47.48	52.28	0.27
Fe05_Light	0.95	1.66	30.59	33.44	32.63	0.29	0.43	33.21	33.73	32.63
Fe05_Light	0.27	1.81	41.52	34.48	18.12	3.57	0.23	43.60	38.05	18.12
Fe05_Light	8.20	13.45	15.09	29.41	29.81	3.20	0.85	36.73	32.61	29.81
Fe15_Dark	21.47	0.96	1.99	31.11	25.97	18.44	0.06	24.42	49.55	25.97
Fe15_Dark	21.21	1.19	2.46	31.15	25.67	18.26	0.06	24.87	49.41	25.67
Fe15_Dark	21.50	1.06	2.36	31.35	25.92	17.77	0.05	24.92	49.12	25.92
Fe15_Dark	21.33	1.09	2.41	31.28	25.94	17.91	0.05	24.82	49.18	25.94
Fe15_Dark	21.28	1.06	2.03	31.12	26.19	18.27	0.06	24.36	49.39	26.19
Fe15_Grey	1.04	29.69	2.27	33.00	31.82	0.42	1.76	33.01	33.41	31.82
Fe15_Grey	2.50	27.90	2.97	32.64	31.31	0.78	1.90	33.37	33.42	31.31
Fe15_Grey	2.01	28.40	2.44	32.81	31.71	1.11	1.52	32.85	33.92	31.71
Fe15_Light	0.66	2.32	30.36	33.11	32.09	0.24	1.23	33.34	33.35	32.09
Fe15_Light	1.34	3.17	28.79	33.09	32.90	0.19	0.52	33.29	33.28	32.90
Fe15_Light	3.80	6.50	22.85	33.05	32.22	0.74	0.82	33.16	33.79	32.22
Fe15_Light	2.55	5.04	25.93	32.71	32.29	0.39	1.09	33.51	33.10	32.29
Fe15_Light	3.28	5.91	23.70	33.04	31.63	1.09	1.35	32.89	34.13	31.63

Table S1. Chemical composition of various phases in $Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_x)Sn_{0.975}Sb_{0.025}$ estimated from multiple points of electron microprobe analysis (EPMA), given in at %.

*Number after Fe in sample name indicates the atomic percent of extra Fe; 'Dark' 'Grey' and 'Light' indicate the contrasts of phases in the back scatter image (BSE), which correspond to Ti-rich, Zr-rich and Hf-rich phases, respectively; 'BDL' means concentration below detection limit.

Table S2. Mole fraction, v (%), of the (Ti,Fe)-rich phase in various $Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_x)Sn_{0.975}Sb_{0.025}$ samples quantified using the Image J software compared to the mole fraction of the (Ti,Fe)-rich phase anticpated from the chemical reaction (1), along with other (Ti,Fe)-rich phase characteristics collected by ImageJ.

		Total Area	Average Size	Max Size			
Sample	Counts	[µm²]	[µm²]	[µm²]	ν_{obs}	ν_{calc}	$ \Delta v /v_{calc}$
TZHNSS_0Fe	73	25887.6	354.6	2093.7	3.6	-	-
TZHNSS_5Fe	37	10830.5	292.7	1179.9	1.5	6.9	0.78
TZHNSS_10Fe	150	68794.5	458.6	3371.4	10.8	13	0.17
TZHNSS_15Fe	180	110540.2	614.1	8658.5	15.5	18.4	0.16

When processing the BSE images in Image J, a threshold value was set to be 50 μ m² to select the Ti-rich phases, i.e. any dark phase larger than 50 μ m² would be identified as a Ti-rich area.



Figure S1. (a) Powder X-ray diffraction (PXRD) patterns of $Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_x)Sn_{0.975}Sb_{0.025}$ samples and (b) a close-up of the 220 diffraction peak revealing peak splitting that implies phase separation into multiple phases (Ti-rich and (Zr, Hf)-rich) with HH or FH structures.



Figure S2a. Fitting of the 220 peak for the Fe-free $Ti_{0.25}Zr_{0.25}Hf_{0.5}NiSn_{0.975}Sb_{0.025}$ sample, indicating coexistence of Ti-rich, Hf-rich and Zr-rich phases.



Figure S2b. Fitting of the 220 peak for the $Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_{0.02})Sn_{0.975}Sb_{0.025}$ sample, indicating coexistence of Ti-rich, Hf-rich and Zr-rich phases.



Figure S3. Back scattered electron microscopy images of $Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_x)Sn_{0.975}Sb_{0.025}$ samples showing the distribution of (Ti,Fe)-rich (black) and (Zr,Hf)-rich (grey) domains in various composites. The processing of the BSE images with Image-J software enables semiquantitative determination of the fraction of (Ti,Fe)-rich phases within various samples.



Figure S4a. Elemental mapping from selected BSE images of the $Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_{0.02})Sn_{0.975}Sb_{0.025}$ sample showing phase separation into (Ti,Fe)-rich, Hf-rich and Zr-rich phases with uniform distribution of Ni, Sn and Sb. Note the preferential incorporation of the added Fe into the Ti-rich phase to form the magnetic inclusions.



Figure S4b. Elemental mapping from selected BSE images of the $Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_{0.05})Sn_{0.975}Sb_{0.025}$ sample showing phase separation into (Ti,Fe)-rich, Hf-rich and Zr-rich phases with uniform distribution of Ni, Sn and Sb. Note the preferential incorporation of the added Fe into the Ti-rich phase to form the magnetic inclusions.



Figure S4c. Elemental mapping from selected BSE images of the $Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_{0.10})Sn_{0.975}Sb_{0.025}$ sample showing phase separation into (Ti,Fe)-rich, Hf-rich and Zr-rich phases with uniform distribution of Ni, Sn and Sb. Note the preferential incorporation of the added Fe into the Ti-rich phase to form the magnetic inclusions.



Figure S4d. Elemental mapping from selected BSE images of the $Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_{0.15})Sn_{0.975}Sb_{0.025}$ sample showing phase separation into (Ti,Fe)-rich, Hf-rich and Zr-rich phases with uniform distribution of Ni, Sn and Sb. Note the preferential incorporation of the added Fe into the Ti-rich phase to form the magnetic inclusions.



Figure S5. Schematic illustration of the molecular orbital diagrams of TiNiSn half-Heusler phase and selected TiNiFeSn full-Heusler inclusions. ΔE represents the energy offset between the conduction band minima of neighboring HH and FH phases.



Figure S6. Transport properties of $Ti_{0.25}Zr_{0.25}Hf_{0.5}(Ni,Fe_x)Sn_{0.975}Sb_{0.025}$ composites: (a) Hall coefficient and (b) electronic thermal conductivity.

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