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Exploring the negative thermal expansion and magnetocaloric effect in Fe$_2$(Hf,Ti) Laves phase materials

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Abstract

The transition-metal based Laves phase materials represent an extended family of alloys with rich and fascinating physical properties. In this work, we have investigated the negative thermal expansion and magnetocaloric effect in arc-melted and melt-spun Fe$_2$Hf$_{1-x}$Ti$_x$ (x = 0.15, 0.27, 0.30, 0.33, 0.36, 0.40) alloys. For x = 0.30–0.40, two hexagonal phases with different compositions share the same Pb$_3$/mmc lattice symmetry, but have slightly different lattice parameters. The saturation magnetization and Curie temperature both follow a decreasing trend with the average unit-cell volume. For Fe$_2$Hf$_{0.85}$Ti$_{0.15}$ melt spinning improves the saturation magnetization from 48.7 to 59.6 Am$^2$/kg and the magnetic entropy change from 0.46 to 0.54 J/kgK at a magnetic field change of 2 T. These enhanced values are attributed to an improved homogeneity caused by a suppression of phase segregation during rapid solidification. We have utilized neutron powder diffraction and Mössbauer spectroscopy to illustrate the correlation between the magnetic order and the negative thermal expansion in single-phase Fe$_2$Hf$_{0.85}$Ti$_{0.15}$. The magnetic moments of Fe align below 400 K in the $a$-$b$ plane and a moment change for the Fe atoms is responsible for the large volumetric coefficient of thermal expansion of $-25 \times 10^{-6}$ K$^{-1}$ over a wide temperature range of 300–400 K.

1. Introduction

The magnetocaloric effect (MCE) is the caloric response of the lattice on the application or removal of a magnetic field and can be characterized by the magnetic entropy change and the adiabatic temperature change [1,2]. In terms of the energy efficiency and environmental safety of MCE-based magnetic refrigeration, the exploration of new MCE materials and the understanding of the mechanism controlling the magnetic phase transition have attracted much attention in recent decades [3,4]. Many magnetocaloric materials undergoing a magnetostructural or a magnetoelastic transition have been studied, such as Mn-Fe-P-Si [5,6], La(Fe,Si)$_{13}$ [7,8], Ni-Mn-based Heusler alloys [9,10], MnCoGe [11], Fe$_2$(Hf,Ta) [12–14] and Mn$_2$Sb [15–17]. Due to the strong spin-lattice coupling, some of the magnetocaloric materials, such as La-Fe-Si-Co [18], MnCoGe [19], and Fe-based Laves phase materials [20,21], are also considered as potential candidates for negative thermal expansion (NTE) materials, which are in high demand in modern industry for the adjustment of the thermal expansion in materials [22,23]. Among them magnetic Fe-based Laves phase materials combine a spontaneous magnetization with a magnetoelastic lattice volume contribution based on two different Fe atomic sites, which combine the advantages of a high thermal conductivity and good mechanical properties for NTE and magnetocaloric applications [20,14].

MCE materials with a large magnetic entropy change generally show a large change in magnetic moment. It is well known that itinerant electron systems with a large magnetic moment have a larger unit-cell volume. Therefore, a steep change in magnetization for itinerant electron systems is generally linked to a steep change in volume, except for magnetic materials that rather change c/a ratios, which may yet occur without volume change. An interesting example is the Fe$_3$(Hf,Ta) Laves phase compound, which shows a sharp magnetization jump at the ferromagnetic-to-antiferromagnetic phase transition, accompanied by a negative thermal expansion effect [24]. This sharp transition is due to a frustration effect, in which the magnetic moment of the Fe atom at the

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2. Experimental methods

Polycrystalline Fe$_2$Hf$_{1-x}$Ti$_x$ (x = 0.15, 0.27, 0.30, 0.33, 0.36, 0.40) compounds were prepared from high-purity elements (Fe 99.98%, Hf 99.95%, Ti 99.99%) by arc melting. Samples with a total mass of 5 g were melted four or five times, and the button-shaped alloys were flipped over after each melting. Four different heat treatments were tried for Fe$_2$Hf$_{1-x}$Ti$_x$ compounds (see Fig. S1 in Supplementary Material). According to the Rietveld refinement results in Fig. 1 (c) the patterns for the arc-melted Ti0.15, 0.27, 0.33, 0.40), denoted as TiX alloys (where X corresponds to the Ti fraction x). With increasing Ti substitution, the peaks become broader, which is seen in the enlarged region in Fig. 1 (b) and the increased full width at half-maximum (FWHM) of (110) and (003) peaks in Fig. 2(a). All samples crystallize in the hexagonal MgZn$_2$-type structure with P6$_3$/mmc symmetry (space group 194), where the Fe atoms occupy the 2a and 6h sites and the Hf/Ti atoms occupy the 4f site. According to the Rietveld refinement results in Fig. 1 (c) the patterns for the Ti0.15 and Ti0.27 samples can be fitted best as single-phase hexagonal. The other four samples, for example the Ti0.36 sample in Fig. 1 (d) can be fitted best by a two-phase model. These two phases share the same space group 194, but with slightly different lattice parameters. The refined lattice parameters are given in Fig. 2(d). The fraction of the Ti-rich phase P1 increases with increasing Ti content. The average unit-cell volume, based on the fraction of the two phases P1 and P2, decreases linearly with Ti content.

To confirm the presence of phase segregation, the backscattered electron SEM images of the Ti0.36 sample are shown in Fig. 2(b). The dark region refers to the Ti-rich phase, corresponding to P1. The chemical compositions of the matrix and Ti-rich phase are determined by EDS and are found to be Fe$_{60.5}$Hf$_{25.5}$Ti$_{14.0}$ and Fe$_{60.5}$Hf$_{25.5}$Ti$_{14.0}$, respectively. It is found that this phase segregation is difficult to avoid by different heat treatments (see Fig. S1 in Supplementary Material). It is worthwhile to note that in Hf$_{0.6}$Ti$_{0.4}$Fe$_2$ a similar XRD peak broadening is attributed to a phase coexistence of AFM and FM states [26], where the homogeneity is supported by SEM mapping at the scale of 100 μm. A variation in chemical composition at a smaller length scale or in other areas of the samples cannot be excluded [40]. From the inset picture in Fig. 2(c), the annealed Ti0.36 sample (annealed at 1273 K for 134 hours) exhibits significant compositional fluctuations, as indicated from the line-scan profile across the Ti-rich boundaries. The chemical composition of the matrix and the Ti-rich phases are Fe$_{60.5}$Hf$_{25.5}$Ti$_{14.0}$ and Fe$_{60.5}$Hf$_{25.5}$Ti$_{14.0}$, respectively.

The M-T curves in Fig. 3(a) show that the magnetization decreases continuously with increasing temperature for the arc-melted Ti0.15 sample. With decreasing temperature it follows the same trajectory without any thermal hysteresis, which suggests a second-order phase transition from the ferromagnetic to the paramagnetic phase. Fig. 3(b) using a $^{57}$Co(Rh) source. The velocity calibration was performed using an α-Fe foil at room temperature. The source and the absorbing samples were kept at the same temperature during the cryogenic measurements. The Mössbauer spectra were fitted using the Mosswinn 4.0 program [29]. Powder neutron diffraction (ND) data at different temperatures were collected at a wavelength of 1.6672 Å using the ND apparatus PEARL [30] at the research reactor of Delft University of Technology. The crystal structures and the atomic occupancies were refined using the Rietveld refinement method implemented in the Fullprof software package [31–33].
Fig. 1. (a) XRD patterns of arc-melted Fe$_2$Hf$_{1-x}$Ti$_x$(x = 0.15, 0.27, 0.30, 0.33, 0.36). (b) Zoomed-in region between 60 and 90° from (a). (c, d) Rietveld refinement results of the arc-melted Ti0.15 and Ti0.36 samples with the zoomed-in region of 60–80° in the inset graphs.

Fig. 2. (a) Full width at half-maximum (FWHM) of (110) and (003) peaks for arc-melted Fe$_2$Hf$_{1-x}$Ti$_x$(x = 0.15, 0.27, 0.30, 0.33, 0.36, 0.40). Backscattered electron SEM images of (b) arc-melted Ti0.36 sample without any heat treatment and (c) arc-melted Ti0.36 sample annealed at 1273 K for 134 h. (d, e, f) Ti-content dependence of the lattice parameters a and c and the unit-cell volume V. The inset in (f) is the fraction of the Ti-rich P1 phase as a function of the Ti content.
and 3(c) show the $M$-$T$ curves for Fe$_2$Hf$_{1-x}$Ti$_x$ upon heating in a magnetic field of 0.01 T and (c) $M$-$T$ curves of Fe$_2$Hf$_{1-x}$Ti$_x$ upon heating in a magnetic field of 1 T. (d) $M$-$H$ curves for Fe$_2$Hf$_{1-x}$Ti$_x$ at a temperature of 5 K. (e) $T_C$ as a function of the average unit-cell volume of Fe$_2$Hf$_{1-x}$Ti$_x$. (f) $M_s$ as a function of average unit-cell volume of Fe$_2$Hf$_{1-x}$Ti$_x$. DFT calculation results for the Fe$_2$Hf$_{1-x}$Ti$_x$ alloys with: (g) formation energy for the ferromagnetic (FM) and antiferromagnetic (AFM) phase, (h) calculated magnetic moment, and (i) calculated lattice parameters $a$ and $c$ as a function of the Ti content. For the single-phase samples (arc-melted Ti0.15, Ti0.27 and melt-spun Ti0.40), the experimental magnetic moment and lattice parameters are also given for comparison in (h) and (i), respectively.

Fig. 3. (a) $M$-$T$ curves for the Ti0.15 sample. (b) $M$-$T$ curves of Fe$_2$Hf$_{1-x}$Ti$_x$ upon heating in a magnetic field of 0.01 T and (c) $M$-$T$ curves of Fe$_2$Hf$_{1-x}$Ti$_x$ upon heating in a magnetic field of 1 T. (d) $M$-$H$ curves for Fe$_2$Hf$_{1-x}$Ti$_x$ at a temperature of 5 K. (e) $T_C$ as a function of the average unit-cell volume of Fe$_2$Hf$_{1-x}$Ti$_x$. (f) $M_s$ as a function of average unit-cell volume of Fe$_2$Hf$_{1-x}$Ti$_x$. DFT calculation results for the Fe$_2$Hf$_{1-x}$Ti$_x$ alloys with: (g) formation energy for the ferromagnetic (FM) and antiferromagnetic (AFM) phase, (h) calculated magnetic moment, and (i) calculated lattice parameters $a$ and $c$ as a function of the Ti content. For the single-phase samples (arc-melted Ti0.15, Ti0.27 and melt-spun Ti0.40), the experimental magnetic moment and lattice parameters are also given for comparison in (h) and (i), respectively.

and 3(c) show the $M$-$T$ curves for Fe$_2$Hf$_{1-x}$Ti$_x$ ($x = 0.15, 0.27, 0.30, 0.33, 0.36, 0.40$) compounds in a magnetic field of 0.01 and 1 T, respectively. $T_C$ initially decreases linearly with the average unit-cell volume and then stabilizes around 310 K, as seen in Fig. 3(e). Substitution of Hf by Ti decreases the atomic spacing of the Fe atoms and leads to a suppression of the FM order, so that $T_C$ can be tuned between 310 and 390 K by changing the Ti content. A series of $M$-$H$ curves was measured at 5 K, as shown in Fig. 4(d). All samples reach a magnetic saturation at the highest field of 5 T. A significant decrease in saturation magnetization is observed for the Ti0.40 sample due to the lower saturation magnetization from the dominant Ti-rich phase (67%). We employed spin-polarized DFT calculations for the formation energy, lattice parameters and magnetic moment, as shown in Fig. 3(g-i). Two magnetic configurations: (i) ferromagnetic (FM) structure, with the Fe moments at the 2a and 6h sites oriented in the a-b plane and (ii) antiferromagnetic (AFM) structure, with at the 6h site ferromagnetically aligned intralayer Fe magnetic moments and antiferromagnetically aligned interlayer Fe magnetic moments with unordered Fe magnetic moments at the 2a site [13] are considered in our DFT calculations (see Fig. S3 in Supplementary Material). Comparing the formation energy of the two magnetic configurations, the FM structure is the more favourable one. As the Ti content increases, the energy difference decreases (in Fe$_2$Ti the energy difference is merely 6 meV/atom) because the FM is destabilized by the decrease in lattice parameters due to the smaller atomic size of Ti [41]. The total magnetic moment also decreases with increasing Ti content. It is worth noting that the magnetic moment of Fe at the 2a site is more sensitive to the Ti content than that of Fe at the 6h site. This stronger instability of the Fe magnetic moment at 2a site is also reported in Ti$_{0.70}$Sc$_{0.30}$Fe$_2$, as observed by neutron diffraction [42]. The lattice parameter decreases linearly with increasing Ti content. For single-phase samples, the magnitude of the calculated lattice parameter and magnetic moment are in agreement with the values obtained from XRD and SQUID, as shown in Fig. 3(h) and Fig. 3(i). The spin-polarized density of states (DOS) for Fe$_2$Hf$_{1-x}$Ti$_x$ ($x = 0.125, 0.25, 0.375$) is shown in Fig. S4. For an increasing Ti substitution the lattice shrinks and the Fermi energy moves towards a lower energy, resulting in a lower magnetization and a lower $T_C$. The substitution of the Ti atom for the Hf atom brings a peak in the DOS close to the Fermi level, which results in a significant impact on the magnetic interactions.

Phase segregation has also been reported in other Fe-based Laves
Fig. 4. (a) Backscattered electron SEM images and mapping for the melt-spun Ti0.36 (17 m/s) sample. Backscattered electron SEM images and line-scanning profile along the red line (b) for the melt-spun Ti0.36 (17 m/s) sample and (c) for the melt-spun Ti0.36 (22 m/s) sample.

Fig. 5. (a) M-T curves of arc-melted and melt-spun Ti0.40 samples in a magnetic field of 1 T. (b) M-H curves of arc-melted and melt-spun Ti0.40 samples at 5 K. M-T curves upon heating in different applied magnetic fields for (c) arc-melted Ti0.40 and (d) melt-spun Ti0.40 samples. Magnetic entropy change $-\Delta S_m$ calculated from the heating curves for (e) arc-melted Ti0.40 and for (f) melt-spun Ti0.40 samples.
phase materials such as Fe₃(Ηf,Nb) [27,40], where the cause of phase segregation is attributed to the positive mixing energy calculated by DFT. However, this is ruled out for Fe₄(Ηf,Ti), since the formation energy for both the AFM and FM state is about ~9 eV according to the DFT calculation in Fig. 3(g). For Fe₃(Ηf,Ti), the large difference in atom size (7.5%) between Ηf (159 pm) and Ti (147 pm) could be responsible for the phase segregation in high-Ti content samples, since a similar phase segregation was observed in the perovskite oxides Gd₁₋ₓSrₓFeOs₃ [43], which was caused by the large size mismatch of 10% for Gd and Sr ions. Phase segregation is a way to relieve local stresses due to a size mismatch.

As a rapid solidification technology, melt-spinning process is found to suppress phase segregation in Fe₄ΗfₓTi₁₋ₓ samples with a high-Ti content (x = 0.30, 0.33, 0.36, 0.40). Fig. 4(a) shows the homogeneous microstructure for the melt-spun Ti₀.₃₆ sample on the wheel side prepared with a wheel surface speed of 17 m/s. For melt-spinning ribbons, the free side of the ribbon has a lower cooling rate than the wheel side of the ribbon [44]. Therefore, for the Ti₀.₃₆ (17 m/s) sample on the free side, the Ti-rich phase can be seen at the grain boundaries, while it is not observed in Tio.₃₆ (22 m/s) sample. From Fig. 4(b-c), the ribbons are found to be well crystalline with a grain size of about 1–3 μm. Line scanning across the grain boundaries shows that the Ti₀.₃₆ (22 m/s) sample is more homogeneous than the Tio.₃₆ (17 m/s) sample and thus the magnetic transition is sharper than the latter (see Fig. S5(a) in Supplementary Material). Compared to the arc-melting technique, the improved homogeneity in melt-spun samples can be attributed to the fact that the high solidification rate of the melt-spinning process suppresses phase segregation. Therefore, a wheel speed of 30 m/s is used for the melt-spun Ti₀.₄₀ sample.

The XRD pattern of the melt-spun Tio.₄₀ (30 m/s) sample shows a single hexagonal MgZn₂-type phase (see Fig. S6 in Supplementary Material). Fig. 5(a) and 5(b) show the M-T and M-H curves for the arc-melted and melt-spun Tio.₄₀ samples. The Tc (283 K) of the melt-spun Tio.₄₀ sample is lower than that of the arc-melted sample (309 K). This can be explained by the fact that the Ti in the melt-spun sample is more homogeneously distributed than in the arc-melted sample, so in the latter only part of the Ti plays a role in reducing Tc. The increased amount of ferromagnetic contribution at high temperature in melt-spun sample can be ascribed to the anti-site disorder of Fe atoms introduced by the melt-spinning process, which is also observed in (La,Co)(Fe,Si)₁₋₃ [44] and melt-spun Fe₂(Ηf,Ta) [45]. On the other hand, Mₜ increases by 22% from 48.7 Am²/kg in the arc-melted sample to 59.6 Am²/kg in the melt-spun sample due to the more homogeneous microstructure. The magnetic entropy change ΔSₘ shown in Fig. 5(e) and 5(f) is calculated from the isofield magnetization curves in Fig. 5(c) and 5(d) using the Maxwell relation: ΔSₘ(ΔH, T) = \int_{H₀}^{H} \frac{(dM(T,H))}{dT} dH, where we choose H₀ = 0 T. For the arc-melted Ti₀.₄₀ sample, |ΔSₘ| broadens asymmetrically towards the low-temperature region as the magnetic field is increased, whereas the shape of |ΔSₘ| becomes symmetric for the melt-spun sample. The magnetic entropy change |ΔSₘ| under a magnetic field change of 2 T for arc-melted and melt-spun Tio.₄₀ sample is 0.46 J/kgK at 306 K and 0.54 J/kgK at 280 K, respectively. The melt-spun Tio.₄₀ sample generates a 20% higher magnetic entropy change. The value of |ΔSₘ| for arc-melted Tio.₁₅ and Tio.₂₇ samples is calculated to be 1.1 and 1.0 J/kgK, respectively (see Fig. S7(b) and Fig. 5(c) in Supplementary Material). The Arrott-plots of the arc-melted Tio.₁₅ and Tio.₂₇ samples in Fig. S7(c) and S7(d) (Supplementary Material) prove that the phase transitions are of second-order, which is consistent with the broad exothermic and endothermic peaks in the DSC curves (see Fig. S8 in Supplementary Material). The |ΔSₘ| of Fe₂ΗfₓTi₁₋ₓ for a magnetic field change of 2 T is comparable to other Fe-based Laves phase materials with a SOMT, with 0.4 J/kgK in Sc₀.₃₅Ti₀.₆₅Fe₁.₉₅ [46], but it is smaller than Fe-based Laves phase materials with a FOMT, with 1.4 J/kgK in Sc₀.₃₅Ti₀.₆₅Fe₁.₉₅ [46] and 2.3 J/kgK in Fe₂Hf₀.₈₆Ta₀.₁₄ [13].

To analyse the nature of the magnetoeelastic transition in this system, powder neutron diffraction (ND) and Mössbauer spectroscopy were used to study the single-phase arc-melted Tio.₁₅ sample. To eliminate possible strains due to thermal gradients during arc-melting, the sample was quenched into water after annealing at 1273 K for 32 h. A detailed Rietveld analysis was performed to refine the crystal structure and magnetic structure from the neutron diffraction patterns at different temperatures. The diffraction patterns recorded at 573 K (PM phase) and 4 K (FM phase) are shown in Fig. 6(a) and 6(b). The diffraction pattern measured at 573 K is characteristic for the nuclear Bragg scattering (PM phase) and was fitted to the MgZn₂-type phase with P6₃/mmc symmetry. The ND pattern obtained at 4 K shows no additional reflections compared to the paramagnetic diffraction pattern. The analysis of the magnetic reflections indicates that the corresponding magnetic structure is defined by the propagation vector k = (0,0,0), which means that the magnetic unit cell coincides with the crystallographic one [13]. The arc-melted Tio.₁₅ sample shows a ferromagnetic ordering of Fe moments below 400 K, which is in good agreement with the Tc (392 K) from SQUID measurements. The FM ordering only increases the intensity at the nuclear peaks. The magnetic contributions are most pronounced at the (100), (101) and (002) peaks. The magnetic Fe moments were independently refined for the two sites. The best fit corresponds to magnetic moments that lie within the basal plane of the hexagonal lattice. The corresponding FM spin configuration is shown in Fig. 6(c). A summary of the crystallographic parameters and the refined Fe moments at different temperatures is shown in Table 1. The total moment of 3.14 µB/Fe (calculated by 3/2 M₀(392) + 1/2 M₀(273)) obtained from ND at 4 K agrees well with the 3.19 µB/Fe calculated by DFT.

The temperature dependence of the lattice constants a and c, and the unit-cell volume V are displayed in Fig. 6(d,e). The lattice constant c increases continuously, while a only increases slowly from 4 to 300 K and, then decreases from 300 to 400 K and finally increases again from 400 to 573 K. As a result, V decreases abnormally from 300 to 400 K. The drop in lattice constant a is about 0.15%, about half that of Hf₀.₈₆Ta₀.₄Fe₂ [13]. The unit-cell volume of the FM phase is larger than that of the PM phase, and the spontaneous volume magnetostriiction accompanying the second-order magnetic phase transition is estimated to be about ΔV/V = 0.25%. The negative thermal expansion observed from 300 K (171.63 Å³) to 400 K (171.20 Å³) leads to a negative thermal expansion coefficient αₜ = (1/V)(ΔV/ΔT) = -25 × 10⁻⁶ K⁻¹ over a temperature range of 100 K, in agreement with [26]. This negative thermal expansion coefficient is comparable to commercial NTE materials like ZrW₂O₇ (αₜ = -27.3 × 10⁻⁶ K⁻¹, 0–300 K) [47] and PtBTO (αₜ = -19.9 × 10⁻⁶ K⁻¹, 298–763 K) [48] and other Fe-based Laves phase materials like Hf₀.₈₆Nb₀.₂₄Fe₂ (αₜ = -15 × 10⁻⁶ K⁻¹, 150–240 K) [27], and Hf₀.₈₆Ta₀.₂₀Fe₂ (αₜ = -57.6 × 10⁻⁶ K⁻¹, 250–340 K) [20].

The Mössbauer spectra of arc-melted Tio.₁₅ and melt-spin Tio.₄₀ samples are shown in Fig. 7(a-f). The area ratio of the components corresponding to the Fe(6h) and Fe(2a) sites was set to 3:1 [40,49]. Table 2 summarises the fitted parameters for the Mössbauer spectra at different temperatures. The small linewidth (0.4 mm/s) for all sites (except for the relaxing phase) indicates a good quality of fit for the spectra. The similar isomer shift and quadrupole splitting for Fe at the 2a and 6h sites indicates that both sites have a similar electronic state [50]. For the arc-melted Tio.₁₅ sample, the spectrum exhibits a paramagnetic feature at 400 K, which is consistent with the neutron diffraction results. The spectra at 4.2, 120 and 300 K contain two magnetic sub-spectra, attributed to the Fe(6h) and Fe(2a) sites. The hyperfine fields for the Tio.₁₅ sample at 4 K are 19.6 T and 17.2 T at the 6h and 2a sites, respectively. Using a proportionality factor of 14.2 T/µB [51] yields magnetic moments for the Fe(6h) site and the Fe(2a) site of 1.4 µB and 1.2 µB respectively. This is in reasonable agreement with the ND results (see Table 1). At 350 K, the spectrum consists of a sextet magnetic sub-spectrum and a quadrupole doublet, which is considered to be the
which is consistent with the neutron diffraction results in Fig. 8 (b). The simultaneously with increasing temperature, which is different from magnetic hyperfine fields of Fe atoms at the 2\text{Fe} site with position (x, 2x, 1/4) and the Hf/Ti atoms at the 4f site with position (1/3, 2/3, z).

Table 1
Fitted neutron diffraction parameters of the Ti0.15 sample obtained at different temperatures. The lattice structure corresponds to the P6_{3}mcm symmetry (space group 194) with the Fe atoms at the 2a site with position (0, 0, 0) and the 6h site with position (x, 2x, 1/4) and the Hf/Ti atoms at the 4f site with position (1/3, 2/3, z).

<table>
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<th>T (K)</th>
<th>Phase</th>
<th>x(2a)</th>
<th>z(2a)</th>
<th>c/a</th>
<th>M_{Fe}^{(2a)} (μs/f.u.)</th>
<th>M_{Fe}^{(6h)} (μs/f.u.)</th>
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</table>

The temperature dependence of the hyperfine field at the 2a and 6h sites is shown in Fig. 8 (a). It is clear that the compound exhibits a ferromagnetic-to-paramagnetic transition between 350 and 400 K, with a coexistence of the ferromagnetic and the paramagnetic phase (45%) [52]. This coexistence of FM and PM phases is consistent with the ND data at 350 K.

The temperature dependence of the hyperfine field at the 2a and 6h sites is shown in Fig. 8 (a). It is clear that the compound exhibits a ferromagnetic-to-paramagnetic transition between 350 and 400 K, with a coexistence of the ferromagnetic and the paramagnetic phase (45%) [52]. This coexistence of FM and PM phases is consistent with the ND data at 350 K.

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and ωs is found in Fig. 8(f). The magnetic-lattice coupling can quantitatively be described by:

\[ \omega_s(T) = kCM(T) \] [57], where \( k \) and \( C \) are the compressibility and the magneto-volume coupling constant, and \( M \) is the magnetic moment. The constant \( kC \) for the Fe2Hf0.85Ti0.15 sample can be obtained from the slope of the curve in Fig. 8(f). For Fe2Hf0.85Ti0.15, the constant \( kC \) at 4.2 K is calculated to be \( 1.48 \times 10^{-10} \text{ cm}^2/\text{A}^2 \). This value is of the same order of magnitude as those for Fe2Hf0.83Ta0.17 [41] and La(Fe0.86Al0.24)13 [58], which are potential MCE materials with a strong magnetoelastic coupling. Short-range disorder, either caused by phase segregation in the Fe2(Hf,Ti) system ascribed to the large difference in Hf and Ti atoms sizes or due to rapid solidification, may account for the second-order phase transition in this magnetoelastic material.

### 4. Conclusions

In summary, we have studied the crystal structure, microstructure, and magnetic properties of arc-melted and melt-spun Fe2Hf1-xTx (x = 0.15, 0.27, 0.30, 0.33, 0.36, 0.40) alloys, which are derived from two isosstructural HfFe2 and TiFe2 Laves phase materials. Surprisingly, a phase segregation is found in samples with \( x = 0.30 \)–\( 0.40 \), which we attribute to the 7.5% size difference between Hf and Ti. The high cooling rate achieved by melt-spinning at a wheel speed of 30 m/s yields homogeneous alloys. The magnetic transition temperature decreases linearly with the average unit-cell volume. The saturation magnetization suppressed by phase segregation can be recovered from 48.7 Am2/kg to 59.6 Am2/kg by melt spinning and thus the magnetocaloric effect can be enhanced from 0.46 to 0.54 J/kg K under a magnetic field change of 2 T due to the improved homogeneity. ND results reveal that the magnetic moments lie within the a-b plane, and the reduction in magnetic moment

![Fig. 7. Mössbauer spectra of the arc-melted Ti0.15 sample at (a) 4.2 K, (b) 120 K, (c) 300 K, (d) 350 K, (e) 400 K. (f) Mössbauer spectra of the melt-spun Ti0.40 sample at 4.2 K. The black line represents the experimental spectrum.](image_url)
of the Fe atoms is consistent with the abnormal decrease in the lattice parameter \(a\) with increasing temperature. We observe a negative thermal expansion \((-25 \times 10^{-6} \text{ K}^{-1})\) for the single-phase \(\text{Fe}_{0.86}\text{Hf}_{0.14}\text{Ti}_{0.15}\) compound over a wide temperature range of 300–400 K. The relation between the negative thermal expansion and the magnetism is discussed by quantitatively analysing the correlation between the spontaneous magnetostriction and magnetic moment of the Fe atoms. Our results provide a significant insight into the magnetoelastic coupling in these magnetocaloric materials and provide an experimental route to solve common fabrication problems in Fe-based Laves phase materials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials


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