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Bulk-like first-order magnetoelastic transition in FeRh particles

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ABSTRACT

Near-equiatomic, chemically-ordered iron-rhodium (FeRh) alloy is a fundamentally interesting material that may become useful in niche applications making use of its unique magneto functional phenomena, for example, the giant inverse magnetocaloric effect near room temperature that is associated with a sharp first-order magnetic phase transition. The nearly discontinuous antiferromagnetic-ferromagnetic phase transformation in bulk FeRh is well-known; however, the transition broadens considerably in fine particles and films with thickness less than 50 nm, precluding their potential applications. Here, we report an abrupt, bulk-like first-order magnetoelastic transformation in powders consisting of sub-micron particles of nearly equiatomic FeRh compound synthesized via solid-state mechanochemical co-reduction of FeF₂ and RhCl₃ and subsequent heat treatments. We demonstrate that annealing at temperatures ranging from 600° C to 800° C enables tailoring phase content, particle size, and magnetic properties of the powders. A maximum magnetic-field-induced entropy change of ~10 J/kg K at $\mu_0\Delta H = 1$ T has been achieved in powders annealed at 800° C. The retention of extraordinary responsiveness in sub-micron particles of FeRh is likely to open doors for system component fabrication using additive manufacturing methods, along with new opportunities to employ FeRh in theranostics.

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1. Introduction

Discontinuous first-order magnetic phase transitions (FOMPTs) are commonly observed when magnetic and crystallographic phase transformations in solids occur in tandem due to the strong interplay between the spins and orbitals of the magnetic moment-carrying species and the underlying crystal lattice [1]. Over the years, first-order magnetic phase transitions have been connected to a number of potentially functional phenomena, such as giant magnetoresistance and giant magnetocaloric effects, unusually strong magnetostriction, and magnetic shape-memory effects, leading to a steady rise of interest in discovery, synthesis, processing, and characterization of materials that exhibit FOMPTs [2–8]. Hence, a fundamental understanding of the mechanisms of such transitions in various compounds and how materials respond to external stimuli, including temperature, pressure, and magnetic field, applied individually or in concert, was and remains the focus of numerous studies.

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It is typical for first-order magnetic (dis)order-order transformations to coincide with changes in chemical bonding as well as the symmetry of crystal lattice, and those cases are known as magnetostructural transitions (MSTs). Among various classes of materials that exhibit first-order MSTs, notable examples include $Gd_5(Ge_xSi_{1-x})_4$ when $x \cong 2$ [9,10], stoichiometric and off-stoichiometric Ni_2MnX (Heusler) compounds, where X = p-block metal or metalloid [11], and MnTX, where T = Ni, Co, and Fe [12–14]. On the other hand, FOMPTs may also occur without changes in crystallographic symmetry across the corresponding magnetic transitions despite discontinuous changes in phase volume. Those kinds of FOMPTs, commonly known as magnetoelastic transitions (METs), are observed in a handful of materials, mostly transition metal-based, such as MnFeP_{1-x}As_x [15], La(Fe_{1-x}Si_x)₁₃ and their hydrides [16], and FeRh [17] at or close to room temperature, although they have also recently been discovered in certain other lanthanide-based compounds, such as R₂In, where R is light lanthanide [18,19]. In general, first-order MSTs and METs are associated with thermomagnetic hysteresis, which becomes an impediment for applications where complete reversibility of an FOMPT is desired [20].

There is a general consensus that the hysteresis is considerably lower and easier to tailor in materials exhibiting first-order METs

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when compared to those that exhibit MSTs, fueling efforts focused on design and manipulation of the former by chemical substitutions, hydrostatic pressure and uniaxial strain, magnetic field, and temperature [20]. Further, effects of processing, more specifically effects of particle size on FOMPTs is a topic of both fundamental and applied interest because exploitation of magneto-functional properties in certain applications requires particles of active materials with sizes ranging from nanometers to micrometers, biomedical applications being a prime example [17,21–23]. Compounds demonstrating FOMPTs are attractive for theranostic applications that involve magnetic resonance imaging [21], in vivo magnetic resonance thermometry [23], controlled delivery and release of drugs [22,24], and cancer therapy via magnetic hyperthermia [22]. Particle size reduction, however, commonly affects both MSTs and METs, broadening the transitions substantially and, in some cases, completely hindering them [25–34]. Fabrication of materials in the form of particles that retain sharp FOMPTs present in their bulk parents is indeed a known materials science challenge. Thus one of the objectives of this work is to demonstrate that carefully designed synthetic routes can address this long-standing issue by focusing on the nearly equiatomic FeRh particles and assessment of their structural and magnetic properties.

As summarized by Swartzendruber [35], a total of five different phases exist in the binary Fe – Rh system. They are listed in Table 1 together with their basic crystallographic information and groundstate magnetic properties; the corresponding phase diagram is reproduced in Fig. S1, Supplemental Information. The phase of interest is a nearly equiatomic α "-FeRh that contains between 47 and 53 at% Rh and crystallizes in an ordered CsC1-type structure, also known as the B2 structure. The α " phase has an antiferromagnetic (AFM) ground state and it displays a reversible, hysteretic FOMPT between the AFM and FM states near room temperature [36]. The AFM \leftrightarrow FM transition on heating (cooling) is accompanied by an isotropic expansion (contraction) of the unit cell volume by ~1% without changing crystal symmetry [37] and with a significant, 5.1 J/g, latent heat [38]. The temperatures of the AFM \leftrightarrow FM magnetic transition during heating and cooling match the corresponding elastic structural transition temperatures, hence the AFM ↔ FM phase transformation in α "-FeRh is first-order MET; hereafter, the temperature at which the MET occurs will be referred as T_t .

The magnetoelastic transition in α "–FeRh is sensitive both to hydrostatic pressure (P) and magnetic field (*H*): T_t increases with the application of hydrostatic pressure with $\frac{\partial T_t}{\partial P} = 5$ K/kbar, and it decreases with the application of magnetic field at a rather high rate of $\frac{\partial T_t}{\partial H} = -8$ K/T [39,40]. The magnetoelastic response of the system is sensitive to the presence of impurities [41]. Among important functional properties that continue to draw research interest to α "–FeRh are giant caloric effects that can be actuated near room temperature by application and removal of magnetic field and/or pressure [41–44]. Direct measurements of the inverse magnetocaloric effect in Fe₅₁Rh₄₉ alloy reveal adiabatic temperature change as high as $\Delta T_{ad} = -12$ K upon first application of the magnetic field $\mu_0\Delta H = 1.9$ T [45] and $\Delta T_{ad} = \pm 6.5$ K during repeated cycling between 0 and 1.9 T [46]. Those adiabatic temperature changes are among the highest reported near room temperature for any magnetocaloric material in the same magnetic field.

Although considerable work has been performed using α "–FeRh in bulk, thin film and composite forms [47], research on micro- or nanoparticles of the same remains in its infancy. As reported in [27,28,31] nearly equiatomic, ~20–50 nm and 100–200 nm FeRh nanoparticles synthesized, respectively, via polyol co-reduction and solid phase reduction methods, undergo hysteretic magnetic transitions at composition-dependent $T_{\rm t}$ s ranging from 320 to 400 K. The transformations are broad, spanning 50–100 K, and the reported magnetic property data reveal that substantial ferromagnetic

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Phase Nature;					
	concentration of Rh in at%	Crystal structure, space group and (Strukturbericht symbol)	Lattice parameters at room temperature (Å)	Ground state magnetism	Phase stability
δ Limited	solid solution of Rh in Fe; 0–3	Body-centered cubic (<i>bcc</i>), <i>lm</i> 3 <i>m</i> (A2)	The phase only exists at high temperature	1	> 1390°C
γ Continu 0–100 o	ous or limited solid solution; 53-100	Face-centered cubic (fcc), Fm3m (A1)	3.759–3.780.	PM	Stable at all temperatures for 53+ at% Rh, otherwise the phase is stable at high temperatures
α Limited	solid solution of Rh in Fe; 0–19	Body-centered cubic (bcc), Im3m (A2)	2.856–2.899	FM	Stable below 750°C in the Fe-rich region; Curie temperature is in the range 760–780°C; transforms to γ upon heating
α' Interme	diate phase; 11–55	CsCl-type (partially ordered away from 50% Rh), <i>Pm</i> 3 <i>m</i> (<i>B</i> 2)	2.929–2.981	FM	Curie temperature is in the range ~300–750 °C; transforms to γ upon heating.
α" Interme	diate phase; 47–53	CsCl-type, <i>Pm</i> 3 <i>m</i> (<i>B</i> 2)	2.978–2.986	AFM	Upon heating, reversibly transforms to FM α' in the range 0–150 $^\circ\text{C}$

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Fig. 1. Room-temperature powder XRD patterns of (a) AM-FeRh, (b) S1, (c) S2, and (d) S3.

contributions – features that may be attributed to chemical inhomogeneity, wide particle size distribution, or/and surface oxidation – persist far below T_t . Further, Hillion et al. [48] and Dupuis et al. [49] found that 3–5 nm FeRh nanocrystals remain FM down to temperatures as low as 3 K, hence the known Fe – Rh phase diagram does not apply to alloy particles reduced to this length scale. Considering published data, preserving the sharpness of the MET characteristic to bulk α "–FeRh in fine particles remains an unresolved challenge. Here we demonstrate a solid-state mechanochemical redox synthesis of fine alloy powders with a nominal composition of Fe₄₉Rh₅₁ that exhibit a nearly discontinuous first-order MET similar to its bulk counterpart.

2. Experimental methods

In a mechanochemical redox syntheses, a mixture of metal salts is milled together with suitable reductants enabling synthesis of nano to sub-micron particles of otherwise difficult to synthesize materials, particularly ductile alloys like FeRh. This bottom-up powder preparation route provides good compositional and particle size control, and it affords unique microstructures, which significantly influence physical properties of the product [50]. As implemented here, during the first step of the synthesis, anhydrous metal halide salts, FeF₂ (98% pure, Alfa Aesar) and RhCl₃ (98% pure, MilliporeSigma), were combined in the desired molar Fe:Rh ratio of 49:51 in an agate mortar. The thoroughly ground reagents were mixed with a stoichiometric amount of metallic Li (99.9% pure, MilliporeSigma) used as a reductant and sealed in a hardened steel milling vial along with the milling media (two 8 mm and six 3 mm stainless steel balls) under argon atmosphere. Milling was performed using a SPEX 8000 shaker mill housed inside an argon-filled glove box to reduce the adventitious oxidation of freshly reduced metals. The combined precursors were milled for 100 min, briefly pausing the milling to dislodge any material from the walls and the corners with a spatula and ensure homogeneous dispersion of salts

and Li-metal. The as-milled powder product was washed with a 50:50 v/v water-ethanol solution to remove the LiF and LiCl byproducts as well as unreacted precursors, resulting in about 75% yield of Fe–Rh alloy powder. Hereafter, the product obtained after washing of as-milled powder is referred to as "AM-FeRh". A part of AM-FeRh was annealed at 600 °C for seven days in an evacuated and sealed quartz tube followed by quenching the tube in a mixture of ice and water. This sample (S1 hereafter) was subjected to further annealing at 700 °C (S2) and, finally, S2 was annealed at 800 °C (S3), each for additional seven days, followed by ice-water mixture quenching. The AM-FeRh and all three annealed powder samples are stable in air and were handled as such.

Room-temperature powder X-ray diffraction (XRD) measurements of all samples were performed using a Philips X'Pert Pro diffractometer with Cu K α_1 radiation. Rietveld refinements using GSAS II were used to quantify the phases present and determine their cell parameters [51]. The refinements converged to goodness of fit, χ^2 < 3, and weighted profile residuals, R_{wp} < 10%. The elastic transition was probed with temperature-dependent powder XRD measurements using a Rigaku TTRAX system equipped with a rotating anode Mo K α source and a high-temperature attachment. The data were collected on heating in dynamic vacuum in the temperature range between 300 and 430 K. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) examinations were performed using an FEI Teneo Lovac field-emission SEM and Oxford Aztec system with X-Max 80 detector to, respectively, determine morphology and quantify elemental compositions. Particle sizes were analyzed with ImageJ using the SEM micrographs according to the ISO 13322-1 standard [52].

Isofield temperature-dependent magnetization measurements were performed using a Superconducting Quantum Interference Device (SQUID) Magnetic Property Measurement System (MPMS) manufactured by Quantum Design Inc. Each sample was cooled down to 5 K in the applied magnetic field of 2 T, and then magnetization data were collected during heating and subsequent cooling

Table 2

Phase fractions (wt%), calculated cubic lattice constants, a (Å), and particle sizes of as-milled (AM-FeRh) and annealed (S1-S3) FeRh powders.

Sample	Phase, wt%	Lattice parameter a, Å	Particle size
AM-FeRh (as-milled and washed)	B2-FeRh, 30%	2.982 (3)	Not measured
	A1-FeRh, 45%	3.799 (2)	
	A1-Rh, 18%	3.764 (4)	
	Fe ₃ O ₄ , 6%	8.369 (2)	
S1 (600 °C)	B2-FeRh, 100%	2.987 (1)	287-319 nm
S2 (700 °C)	B2-FeRh, 79%	2.987 (2)	370-395 nm
	A1-FeRh, 15%	3.772 (2)	
	A1-Rh, 6%	3.798 (4)	
S3 (800 °C)	B2-FeRh, 76	2.988 (2)	0.6–1.1 μm
	A1-FeRh, 24%	3.768 (4)	

in the same field, respectively designated as field cooled warming (FCW) and field cooled cooling (FCC) protocols. The MET temperatures were assigned as the temperatures corresponding to the maxima of the temperature derivative of M(T) recorded in FCW protocols. Magnetic properties of S3 were examined in detail because this material exhibits the sharpest first-order MET and the narrowest hysteresis. The isothermal magnetic field-induced entropy changes, Δ S, of sample S3 were quantified using M(T) data measured between 300 and 395 K during FCW in constant magnetic fields ranging between 0.01 and 5 T using Maxwell relation [53] and Clausius-Clapeyron equation [54].

3. Results

3.1. Structural properties of as-milled and annealed FeRh powders

The Rietveld refinements of structure models using room-temperature powder XRD patterns of all samples are shown in Fig. 1, with the results of Rietveld analyses listed in Table 2. The Bragg peaks observed in the AM-FeRh powder, Fig. 1(a), reflect a mixture of four phases – B2-FeRh, A1-FeRh, A1-Rh, and iron oxide, Fe₃O₄, with the first two being the major phases. Since the milling was performed in oxygen-free atmosphere, a minor amount of Fe₃O₄ likely formed when reduced Fe nanoparticles unreacted with Rh are exposed to air before washing. Significant broadening of the Bragg peaks indicates either or both non-equilibrium or nanocrystalline nature of the reaction product [55]. Annealing AM-FeRh at 600 °C followed by quenching (sample S1) facilitates further reactions between the multiple phases present in the as-milled FeRh sample, leading to the formation of a single-phase (within the accuracy of powder XRD method) material with an ordered B2-type crystal structure and lattice parameter a = 2.987(1) Å. Contrary to AM-FeRh, the minor Fe₃O₄ impurity is no longer seen in the XRD pattern of S1 and other annealed samples. Considering that small quantities of unreacted Li embedded inside agglomerates of as-reduced nanoparticles were inaccessible to water-ethanol mixture during the washing, the first annealing feasibly reduces Fe₃O₄ to elemental iron $(Fe_3O_4 + 8Li \rightarrow 4Li_2O + 3Fe)$ that further reacts with Rh-containing species at 600 °C to form B2-FeRh. The formed Li₂O reacts with moisture present in air, forming X-ray amorphous LiOH·nH₂O.

The Bragg peaks of S1 are narrow, suggesting much improved crystallinity and chemical homogeneity when compared to AM-FeRh. Additional annealing of S1 at 700 °C and quenching (S2) results in precipitation of A1-FeRh (~15 wt%) and elemental Rh (~6 wt%), the remainder (~79 wt%) being the B2 phase, Fig. 1(c) and Table 2. Finally, upon additional annealing of S2 at 800 °C and quenching (S3), a redistribution of Rh into either or both B2- and A1-FeRh lattices is noted, such that the concentration of phase with the B2 crystal structure with a = 2.988(2) Å decreases from 79 to 74 wt% and the concentration of A1-FeRh phase with a = 3.768 (4) Å increases to 26 wt%. Micrographs obtained via secondary electron imaging were acquired for each of the heat-treated samples and they are shown in Fig. 2. There is a minor increase in the average particle size (Table 2)

from 287 to 319 nm for S1 (a) to 370–394 nm for S2 (b), and a substantial increase in size up to 0.6–1.1 μ m with visible necking for S3 (c). These changes are consistent with the increase in the cumulative annealing time and higher annealing temperatures.

3.2. Development of magnetoelastic transition in FeRh powders by annealing

Temperature dependencies of magnetization, *M*(T), measured in an applied magnetic field of 2 T are shown in Fig. 3. Magnetization of AM-FeRh monotonously increases with decreasing temperature, reaching 43 Am²/kg at 10 K as illustrated in the inset of Fig. 3. The absence of AFM \leftrightarrow FM phase transition indicates that chemical composition of the FeRh (B2-type) phase in the as-milled powders is outside the 47 - 53 at% Rh concentration range required for the FM α –FeRh \leftrightarrow AFM α "–FeRh transformation to occur. Together with a minor quantity of Fe_3O_4 and likely presence of X-ray amorphous phase(s) this explains a significant ferromagnetic component manifested in the M(T) data. Upon annealing at 600 °C, S1 demonstrates a steep rise of magnetization during the FCW measurement, revealing AFM \rightarrow FM transition centered at 380 K (Fig. 3) and indicating the presence of the B2 α "–FeRh phase at low temperatures. A substantial, near-constant 25 A m^2/kg magnetization, M_{const}, is observed up to ~350 K, suggesting coexistence of AFM α"-FeRh and FM α' -FeRh in this region. Subsequent cooling results in a sluggish reverse FM \rightarrow AFM phase transformation that spans over 250 K, resulting in very broad thermomagnetic hysteresis between the M(T)curves recorded using FCW and FCC protocols. When compared with S1, S2 that was annealed at 700° C demonstrates a minor reduction of the AFM \rightarrow FM transition temperature, from 380 K to T_t = 368 K during the FCW measurement, a faster but still slow reverse FM \rightarrow AFM transition that spans across ~150 K, a narrower but still broad thermal hysteresis, and a decreased $M_{const} = 19 \text{ A m}^2/\text{kg}$.

The sluggish MET behaviors seen in the cooling branches of the magnetothermal curves recorded for S1 and S2 are reminiscent of magnetic properties of nearly equiatomic FeRh nanoparticles and thin films reported in the past [27,28,31,32,56]. In systems with reduced dimensionality, the nucleation of a new phase during diffusion-less structural transition is often hindered by a large concentration of surface defects [57,58]. These defects lead to high interface energy barriers between the parent and incipient phases and, thus, slow down the kinetics of growth of the new phase [59]. Upon annealing, the surface defects are reduced, which in turn reduces the interface energy and, thus, a systematic decrease of thermomagnetic hysteresis is observed when the annealing temperature increases. Indeed, annealing at 800°C leads to a nearly discontinuous AFM \rightarrow FM transition observed at 336 K during heating and a much narrower thermal hysteresis width of 15 K, comparable to that of bulk FeRh [40,42], that is due to a much faster reverse FM \rightarrow AFM transformation on cooling. Below T_t, M_{const} becomes negligibly small, in line with the absence of ferromagnetic α' -FeRh in this material (Table 2).

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Fig. 2. Secondary electron micrographs of FeRh powders heat-treated at (a) 600 °C (S1), (b) 700 °C (S2), and (c) 800 °C (S3). The scale bars are 5 µm.



Fig. 3. Temperature dependencies of magnetization, M(T), for the heating (FCW) and cooling (FCC) measurements in applied magnetic field of $\mu_0 H = 2 T$; arrows indicate the directions of temperature change. Inset shows M(T) of AM-FeRh measured on heating in the same 2 T field.

The annealing – structure – magnetic behavior results described above could be reconciled considering the published Fe – Rh phase diagram, Fig. 1(S) in the Supplemental, and previous reports describing the effects of heat treatments near the 50:50 (molar) concentration. Bulk, nearly equiatomic as-cast FeRh alloys are usually heat treated in the range 800 – 1000 °C to achieve homogenization and crystallographic ordering [47]. According to the phase diagram, $B2 \alpha'$ –FeRh that has Curie temperature between ~300 and 400 °C and

undergoes a first-order MET to α "-FeRh near room temperature, is stable in the near-equiatomic range of concentrations in this temperature regime, while the paramagnetic fcc γ -solid solution (the A1 phase) exists in the whole range of Rh compositions at higher temperatures. Several studies, however, suggest that this part of the phase diagram may be imprecise due to the unexpected appearance of high-temperature A1-FeRh in the composition range where only α' -FeRh should exist [60–62]. The discrepancies were clarified experimentally by Takahashi and Oshima [62] and then again by Chirkova et al. [46] via examination of the effect of annealing time and temperature on the phase composition of bulk FeRh. Both reports suggest that annealing at high temperatures for prolonged periods of time decreases the MET temperature T_t of α –FeRh due to precipitation of Rh out of the ferromagnetic α phase by diffusion and consequent growth of Rh-rich A1-FeRh. Our results are in agreement with these observations since as follows from Table 2 and Fig. 3, the concentration of the A1-FeRh phase in the annealed powders increases from 0 (S1) to 15 (S2) and 24% (S3), while $T_{\rm t}$ decreases by 44 K (from 380 to 368 and then finally to, 336 K) as the annealing temperature goes up from 600° to 800°C.

First-order MET of nearly equiatomic α' -FeRh powders is highly sensitive to the magnetic field, shifting to lower temperatures as shown in Fig. 4(a) for S3. Similarly, isothermal magnetization data, shown in Fig. 4(b), reveal field-induced transitions from the lowfield AFM to high-field FM phase occurring at different temperature-



Fig. 4. (a) Isofield magnetization of S3 recorded during heating in magnetic fields between 0.01 and 5 T; (b) isothermal magnetization of S3 measured at temperatures ranging from 290 K to 370 K, with only field-up data shown for clarity.



Fig. 5. Temperature variation of the critical field, H_{crit} , required to induce the AFM \rightarrow FM transition in S3. Data for arc-melted bulk FeRh from Ref [40] are included to illustrate a similar behavior. All curves are fitted to the relation, $H_{crit} = H_0 \{1 - (T/T_0)^2\}$.

dependent critical magnetic fields, H_{crit} . The magnetic field dependence of T_t and temperature dependence of H_c are typical features of the first-order MET reliably established in bulk nearly equiatomic α' –FeRh [36,40]. Consistent with previous reports in the literature, T_t varies linearly with the temperature at a rate of $dT_t/dH \cong -8K/T$ [36]. The relationship between H_{crit} and temperature, shown in Fig. 5, is governed by the equation: $H_{crit} = H_o \{1 - (T/T_o)^2\}$ [36,40], where H_o is the value of the magnetic field at 0K and T_o is the transition temperature at zero magnetic field. For Sample S3, H_o and T_o was determined as 485 kOe and 352 K, respectively. For reference, data from previous literature reports on bulk nearly equiatomic FeRh alloys are also included in Fig. 5.

Last, it is well established that the AFM \leftrightarrow FM transformation in bulk α – FeRh is coupled with the abrupt cell volume change, $\Delta V/V$ \approx 1%, while retaining its cubic B2-ordered crystal structure [63]. To verify whether a similar structural change occurs in fine particles synthesized via mechanochemical redox reaction from iron and rhodium salts, powder XRD measurements were performed in the temperature range of 303-433 K using S1 as a phase-pure representative of the series. The contour plot shown in Fig. 6 clearly reveals the occurrence of an isostructural phase transition with $\Delta a/a$ ~ 0.28%, in agreement with published literature describing bulk materials [63]. Since T_t is suppressed by magnetic field, the structural transition temperature observed in the powder XRD data is higher than the same deduced from M(T) data measured at 2T (Fig. 3). Considering dT_t/dH is -8 K/T, the AFM to FM phase transition temperature in the absence of magnetic field is expected to occur close to 400 K, in good agreement with $T_{\rm t}$ determined from the XRD study, where the two phases coexist between ~395 and 410 K, and



Fig. 6. Behavior of the (112) Bragg peak in S1 as function of temperature during heating, clearly indicating a discontinuous phase transition centered at ~403 K in zero applied magnetic field.



Fig. 7. The temperature dependence of ΔS for $\mu_0 \Delta H = 1$ T calculated for S3 from magnetization data presented in Fig. 4 using methods based on the Clausius-Clapeyron [54] and Maxwell equations [53].

403 K is the transition midpoint (Fig. 5). Combined with magnetization data illustrated in Fig. 3, these results confirm the occurrence of first-order MET in S1. Considering that M(T) behavior of samples S2 and S3 is qualitatively similar to S1 and that magnetic transitions for those samples are sharper (Figs. 3, 4), we conclude that the same first-order MET takes place in all heat-treated powders.

3.3. Magnetocaloric effect

When the magnetic transition is extremely sharp and when it remains sharp as the magnetic field increases, a large, that is, giant magnetocaloric effect is expected. In this regard, the transition observed in S3 during the FCW measurement is a virtually discontinuous change in magnetization that occurs in the 2T magnetic field presenting, essentially, the case of a nearly ideal FOMPT. We first evaluate the MCE of S3 by calculating ΔS using the Clausius-Clapeyron equation and M(T) data of Fig. 4(a) recorded under different magnetic fields, following methodology described earlier [54]. The temperature dependence of ΔS for $\mu_0 \Delta H = 1$ T peaks around 10 J/ kg K at ~345 K, and is illustrated in Fig. 7. Considering that the changes of magnetization with temperature both before and after the transition are minimal (Fig. 4), the maximum value of the magnetic field-induced ΔS defines the total entropy change across FOMPT. Hence, increasing $\mu_0 \Delta H$ beyond 1 T will have only a minor effect on the peak value of ΔS , but the temperature span across which the large ΔS is observed widens as shown in Fig. S2, Supplementary Information. Such an increase in temperature span of large ΔS is also observed in a previous study on the equiatomic FeRh [64] and is characteristic of materials exhibiting giant magnetocaloric effects associated with FOMPTs [65]. The $\Delta S(T)$ calculated from the same set of M(T) data using the Maxwell relation [53] matches that obtained using the Clausius-Clapeyron equation within experimental errors. The observation of a nearly ideal first-order MET in FeRh powders synthesized in this work is promising, considering that the giant MCE in the vicinity of the transition reaches ΔS of 10 J/ Kg K for $\mu_0 \Delta H$ = 1 T. The maximum entropy change demonstrated by the powders is among the largest values reported for any material in fine-particle form [66].

4. Conclusions

Successful synthesis of *B2*-ordered α'/α'' -FeRh powders with fine particles that exhibit a sharp first-order magnetoelastic transition near room temperature is demonstrated via solid-state mechanochemical redox synthesis and subsequent heat treatments. Overall, this study presents the ability to control phase composition, microstructure, and physical behavior of FeRh particles using the mechanochemical synthesis. The relative stabilities of three different phases, α' , α'' , and γ , in the powder with a near-equiatomic overall composition, were evaluated and their presence correlated to the magnetic, crystallographic and magnetocaloric properties of the synthesized materials. We observed a nearly ideal discontinuous first-order MET in fine FeRh particles annealed between 600 and 800 °C, demonstrating that FOMPT can be fully retained in finite-size particles provided the synthesis conditions are optimized. The powders exhibit a large MCE with $\Delta S = 10 \text{ J/Kg K}$ for 1 T magnetic field change, which is among the largest values obtained to date near room temperature for any magnetocaloric material fabricated in the form of submicron particles. Finally, we conclude that bottom-up synthesis approach such as the one demonstrated here can be tailored to obtain high-quality fine particles without losing functionalities detected in the bulk and can easily be extended to other binary, ternary and multinary intermetallic systems.

CRediT authorship contribution statement

Anis Biswas: Investigation, Formal analysis, Writing – original draft. Shalabh Gupta: Conceptualization, Investigation, Formal analysis, Writing – original draft. Dustin Clifford: Investigation, Formal analysis. Yarosalv Mudryk: Formal analysis, Writing – review & editing. Ravi Hadimani: Writing – review & editing. Radhika Barua: Conceptualization, Formal analysis, Resources, Supervision, Writing – original draft, Writing – review & editing. Vitalij K. Pecharsky: Resources, Supervision, Writing – review & editing.

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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2022.165993.

References

- S.B. Roy, First order magneto-structural phase transition and associated multifunctional properties in magnetic solids, J. Phys. Condens. Matter 25 (2013) 183201.
- [2] S.C. Ma, D. Hou, Y.Y. Gong, L.Y. Wang, Y.L. Huang, Z.C. Zhong, D.H. Wang, Y.W. Du, Giant magnetocaloric and magnetoresistance effects in ferrimagnetic Mn_{1.9}Co_{0.1}Sb alloy, Appl. Phys. Lett. 104 (2014) 022410.
- [3] J. Liu, T. Gottschall, K.P. Skokov, J.D. Moore, O. Gutfleisch, Giant magnetocaloric effect driven by structural transitions, Nat. Mater. 11 (2012) 620.
- [4] Y. Lee, Z.Q. Liu, J.T. Heron, J.D. Clarkson, J. Hong, C. Ko, M.D. Biegalski, U. Aschauer, S.L. Hsu, M.E. Nowakowski, J. Wu, H.M. Christen, S. Salahuddin, J.B. Bokor, N.A. Spaldin, D.G. Schlom, R. Ramesh, Large resistivity modulation in mixed-phase metallic systems, Nat. Commun. 6 (2015) 5959.
- [5] L. Morellon, P.A. Algarabel, C. Magen, M.R. Ibarra, Giant magnetoresistance in the Ge-rich magnetocaloric compound, Gd₅(Si_{0.1}Ge_{0.9})₄, J. Magn. Magn. Mater. 237 (2001) 119.
- [6] X. Moya, S. Kar-Narayan, N.D. Mathur, Caloric materials near ferroic phase transitions, Nat. Mater. 13 (2014) 439.
- [7] L. Morellon, P.A. Algarabel, M.R. Ibarra, J. Blasco, B. Garcia-Landa, Z. Arnold, F. Albertini, Giant magnetoresistance near the magnetostructural transition in Gd₅(Si_{1.8}Ge_{2.2}), Appl. Phys. Lett. 73 (1998) 3462.

- [8] L. Morellon, P.A. Algarabel, M.R. Ibarra, J. Blasco, B. García-Landa, Z. Arnold, F. Albertini, Magnetic-field-induced structural phase transition in Gd₅(Si_{1.8}Ge_{2.2}), Phys. Rev. B 58, R14721.
- [9] V.K. Pecharsky, K.A. Gschneidner Jr., Giant magnetocaloric effect in Gd₅(Si₂Ge₂), Phys. Rev. Lett. 78 (1997) 4494.
- [10] L. Morellon, P.A. Algarabel, M.R. Ibarra, J. Blasco, B. Garcia-Landa, Z. Arnold, F. Albertini, Magnetic-field-induced structural transition in Gd₅(Si_{1.8}Ge_{2.2}), Phys. Rev. B 58 (1998) R14721.
- [11] T. Bachaga, J. Zhang, M. Khitouni, J.J. Sunol, NiMn-based Heusler magnetic shape memory alloys: a review, Int. J. Adv. Manuf. Technol. 103 (2019) 2761.
- [12] A. Biswas, A.K. Pathak, N.A. Zarkervich, X. Liu, Y. Mudryk, V. Balema, D.D. Johnson, V.K. Pecharsky, Designed materials with the giant magnetocaloric effect near room temperature, Acta Mater. 180 (2019) 341.
- [13] A. Biswas, N.A. Zarkevich, Y. Mudryk, A.K. Pathak, A.V. Smirnov, V.P. Balema, D.D. Johnson, V.K. Pecharsky, Controlling magnetostructural transition and magnetocaloric effect in multi-component transition-metal-based materials, J. Appl. Phys. 129 (2021) 193901.
- [14] T.Q. Hartnett, V. Sharma, R. Barua, P.V. Balachandran, Density functional theory study of chemical pressure in multicaloric MTX compounds, Appl. Phys. Lett. 118 (2021) 212408.
- [15] O. Tegus, E. Bruck, K.H.J. Buschow, F.R. de Boer, Transition-metal-based magnetic refrigerants for room-temperature applications, Nature 415 (2002) 150.
- [16] A. Fujita, S. Koiwai, S. Fujieda, K. Fukamichi, T. Kobayashi, H. Tsuji, S. Kaji, A.T. Saito, Magnetocaloric effect in spherical La (Fe_xSi_{1-x})₁₃ and their hydrides for active magnetic regenerator-type refrigerator, J. Appl. Phys. 105 (2009) 07A936.
- [17] M.P. Annaorazov, S.A. Nikitin, A.L. Tyurin, K.A. Asatryan, A.K. Dovletov, Anomalously high entropy change in FeRh alloy, J. Appl. Phys. 79 (1996) 1689–1695.
- [18] F. Guillou, A.K. Pathak, D. Paudyal, Y. Mudryk, F. Wilhelm, A. Rogalev, V.K. Pecharsky, Non-hysteretic first-order phase transition with large latent heat and giant low-field magnetocaloric effect, Nat. Commun. 9 (2018) 2925.
- [19] A. Biswas, N.A. Zarkervich, A.K. Pathak, O. Dolotko, I.Z. Hlova, A.V. Smirnov, Y. Mudryk, D.D. Johnson, V.K. Pecharsky, First-order magnetic phase transition in Pr₂In with negligible thermomagnetic hysteresis, Phys. Rev. B 101 (2020) 224402.
- [20] F. Scheibel, T. Gottschall, A. Taubel, M. Friesm, K.P. Skokov, A. Terwey, W. Keune, K. Ollefs, H. Wende, M. Farle, M. Acet, Hysteresis design of magnetocaloric materials—from basic mechanisms to applications, Energy Technol. 6 (2018) 1397-428.
- [21] M. Barbic, S.J. Dodd, H.D. Morris, N. Dilley, B. Marcheschi, A. Huston, A.P. Koretsky, Magnetocaloric materials as switchable high contrast ratio MRI labels, Magn. Reson. Med. 81 (2019) 2238–2246.
- [22] A.M. Tishin, Y.I. Spichkin, V.I. Zverev, P.W. Egolf, A review and new perspectives for the magnetocaloric effect: new materials and local heating and cooling inside the human body, Int. J. Refrig. 68 (2016) 177–186.
- [23] J.H. Hankiewicz, Z. Celinski, K.F. Stupic, N.R. Anderson, R.E. Camley, Ferromagnetic particles as magnetic resonance imaging temperature sensors, Nat. Commun. 7 (2016) 1–8.
- [24] A.S. Komlev, R.R. Gimaev, V.I. Zverev, Smart magnetocaloric coatings for implants: controlled drug release for targeted delivery, Phys. Open 7 (2021) 100063.
- [25] J.S. Blázquez, J.J. Ipus, L.M. Moreno-Ramírez, J.M. Álvarez-Gómez, D. Sánchez-Jiménez, S. Lozano-Pérez, A. Conde, Ball milling as a way to produce magnetic and magnetocaloric materials: a review, J. Mater. Sci. 52 (2017) 11834–11850.
- [26] C. Marquina, M.R. Ibarra, P.A. Algarabel, A. Hernando, P. Crespo, P. Agudo, A.R. Yavari, E. Navarro, Magnetic and magnetoelastic behavior of mechanically alloyed FeRh compound, J. Appl. Phys. 81 (1997) 2315–2320.
- [27] H.Y.Y. Ko, T. Suzuki, N.T. Nam, N.N. Phuoc, J. Cao, Y. Hirotsu, Magnetic and structural characterizations on nanoparticles of FePt, FeRh and their composites, J. Magn. Magn. Mater. 320 (2008) 3120–3123.
- [28] Z. Jia, J.W. Harrell, R.D.K. Misra, Synthesis and magnetic properties of self-assembled FeRh nanoparticles, Appl. Phys. Lett. 93 (2008) 022504.
- [29] J. Feng, R. Geutjens, N. Thang, J. Li, X. Guo, X. Kéri A., A. Schmidt-Ott, Magnetic phase transition in spark-produced ternary LaFeSi nanoalloys, ACS Appl. Mater. Interfaces 10 (2018) 6073–6078.
- [30] A. Biswas, I. Das, C. Majumdar, Modification of the charge ordering in $Pr_{1/2}Sr_{1/2}MnO_3$ nanoparticles, J. Appl. Phys. 98 (2005) 124310.
- [31] Y. Cao, Y. Yuan, Y. Shang, V.I. Zverev, R.R. Gimaev, R. Barua, R.L. Hadimani, L. Mei, G. Guo, H. Fu, Phase transition and magnetocaloric effect in particulate Fe-Rh alloys, J. Mater. Sci. 55 (2020) 13363–13371.
- [32] R. Barua, F.V. Jimenez-Villacorta, J.E. Shield, D. Heiman, L.H. Lewis, Nanophase stability in a granular FeRh-Cu system, J. Appl. Phys. 113 (2013) 17B523.
- [33] A. Biswas, I. Das, Magnetic and transport properties of nanocrystalline Nd_{0.5}Sr_{0.5}MnO₃, J. Appl. Phys. 102 (2007) 064303.
- [34] H. Hu, L. Chen, J. Wang, L. Bao, J.R. Sun, B.G. Shen, Particle size dependent hysteresis loss in La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}C_{0.2} first-order systems, Appl. Phys. Lett. 100 (2012) 072403.
- [35] LJ. Swartzendruber, The Fe Rh (Iron-Rhodium) system, Bull. Alloy Phase Diagr. 5 (1984) 456.
- [36] J.S. Kouvel, C.C. Hartelius, Anomalous magnetic moments and transformations in the ordered alloy FeRh, in: Proceedings of the Seventh Conference on Magnetism and Magnetic Materials, Springer, Boston, MA, 1962, pp. 1343–1344.
- [37] F.D. Bergevin, L. Muldawer, Crystallographic Study of an Iron-rhodium Alloy 252 CR Academy of Science, 1961, pp. 1347–1349.

- [38] D.W. Cooke, F. Hellman, C. Baldasseroni, C. Bordel, S. Moyerman, E. Fullerton, Thermodynamic measurements of Fe-Rh alloys, Phys. Rev. Lett. 109 (2012) 255901.
- [39] A.J. Heeger, Pressure dependence of the FeRh first-order phase transition, J. Appl. Phys. 41 (1970) 4751–4752.
- [40] J.B. McKinnon, D. Melville, D, E.W. Lee, The antiferromagnetic-ferromagnetic transition in iron-rhodium alloysm, J. Phys. C Solid State Phys. 3 (1S) (1970) S46.
- [41] R. Barua, F.V. Jiménez-Villacorta, L.H. Lewis, Predicting magnetostructural trends in FeRh-based ternary systems, Appl. Phys. Lett. 103 (2013) 102407.
- [42] R. Barua, F.V. Jiménez-Villacorta, L.H. Lewis, Towards tailoring the magnetocaloric response in FeRh-based ternary compounds, J. Appl. Phys. 115 (2014) 17A903
- [43] E. Stern-Taulats, T. Castán, A. Planes, L.H. Lewis, R. Barua, S. Pramanick, L. Manosa, Giant multicaloric response of bulk Fe₄₉Rh₅₁, Phys. Rev. B 95 (2017) 104424.
- [44] S.A. Nikitin, G. Myalikgulyev, M.P. Annaorazov, A.L. Tyurin, R. Myndyev, S.A. Akopyan, Giant elastocaloric effect in FeRh alloy, Phys. Lett. A 171 (1992) 234–236.
- [45] S.A. Nikitin, G. Myalikgulyev, A.M. Tishin, M.P. Annaorazov, K.A. Asatryan, A.L. Tyurin, The magnetocaloric effect in Fe₄₉Rh₅₁ compound, Phys. Lett. A 148 (1990) 363–366.
- [46] A. Chirkova, F. Bittner, K. Nenkov, N.V. Baranov, L. Schultz, K. Nielsch, T.G. Woodcock, The effect of the microstructure on the antiferromagnetic to ferromagnetic transition in FeRh alloys, Acta Mater. 131 (2017) 31–38.
- [47] L.H. Lewis, C.H. Marrows, S. Langridge, Coupled magnetic, structural, and electronic phase transitions in FeRh, J. Phys. D Appl. Phys. 49 (2016) 323002.
- [48] A. Hillion, A. Cavallin, S. Vlaic, A. Tamion, F. Tournus, G. Khadra, K. Sato, Low temperature ferromagnetism in chemically ordered FeRh nanocrystals, Phys. Rev. Lett. 110 (2013) 087207.
- [49] V. Dupuis, A. Robert, A. Hillion, G. Khadra, N. Blanc, D. Le Roy, A. Tamion, Cubic chemically ordered FeRh and FeCo nanomagnets prepared by mass-selected low-energy cluster-beam deposition: a comparative study, Beilstein J. Nanotechnol. 7 (2016) 1850–1860.
- [50] T. Tsuzuki, P.G. McCormick, Mechanochemical synthesis of nanoparticles, J. Mater. Sci. 39 (2004) 5143–5146.
- [51] B.H. Toby, R.B. Von, Dreele, GSAS-II: the genesis of a modern open-source allpurpose crystallography software package, J. Appl. Crystallogr. 46 (2013) 544–549.
- [52] Standard ISO 13322-1: 2004 Particle size analysis Image analysis methods Part 1: Static image analysis methods.

- [53] H.N. Bez, H. Yibole, A. Pathak, Y. Mudryk, V.K. Pecharsky, Best practices in evaluation of the magnetocaloric effect from bulk magnetization measurements, J. Magn. Magn. Mater. 458 (2018) 301–309.
- [54] K. Xu, Z. Li, Y.L. Zhang, C. Jing, An indirect approach based on Clausius–Clapeyron equation to determine entropy change for the first-order magnetocaloric materials, Phys. Lett. A 379 (2015) 3149–3154.
- [55] C. Suryanarayana, Mechanical alloying: a novel technique to synthesize advanced materials, Research 2019 (2019) 4219812.
- [56] M.G. Loving, R. Barua, C. Le Graët, C.J. Kinane, D. Heiman, S. Langridge, C.H. Marrows, L.H. Lewis, Strain-tuning of the magnetocaloric transition temperature in model FeRh films, J. Phys. D Appl. Phys. 51 (2017) 024003.
- [57] V. Podzorov, B.G. Kim, V. Kiryukhin, M.E. Gershenson, S.-W. Cheong, Martensitic accommodation strain and the metal-insulator transition in manganites, Phys. Rev. B 64 (R) (2001) 140406.
- [58] A. Biswas, I. Das, Experimental observation of charge ordering in nanocrystalline Pr_{0.65}Ca_{0.35}MnO₃, Phys. Rev. B 74 (2006) 172405.
- [59] Z. Nishiyama, M. Fine, M. Meshii, C. Wayman (Eds.), Martensitic Transformation, Academic, New York, 1978.
- [60] C.F. Sanchez-Valdes, R.R. Gimaev, M. Lopez-Cruz, J.L. Sanchez Liamazares, V.I. Zverev, A.M. Tishin, A.M.G. Carvalho, D.J.M. Aguiar, Y. Mudryk, V.K. Pecharsky, The effect of cooling rate on magnetothermal properties of Fe₄₉Rh₅₁, J. Magn. Magn. Mater. 498 (2020) 166130.
- [61] N.A. Zarkevich, D.D. Johnson, FeRh ground state and martensitic transformation, Phys. Rev. B 97 (2018) 014202.
- [62] M. Takahashi, R. Oshima, Annealing effect on phase transition of equiatomic FeRh alloy, Materials Transaction, JIM J. Intern. Med. 6 (1995) 735.
- [63] L. Zsoldos, Lattice parameter change of FeRh alloys due to antiferromagnetic-ferromagnetic transformation, Phys. Status Solidi (B) 20 (1967) K25–K28.
- [64] M.L. Arreguín-Hernández, C.F. Sánchez-Valdés, J.L. Sánchez Llamazares, D. Ríos-Jara, Vitalij K. Pecharsky, M.I. Blinov, V.N. Prudnikov, B.B. Kovalev, V.I. Zverev, A.M. Tishin, Magnetoelastic transition and magnetocaloric effect in induction melted Fe₁₀₀₋ xRh_x bulk alloys with x= 50, 51, J. Alloy. Compd. 871 (2021) 159586.
- [65] V.K. Pecharsky, K.A. Gschneidner Jr., A.O. Pecharsky, A.M. Tishin, Thermodynamics of the magnetocaloric effect, Phys. Rev. B 64 (2001) 144406.
- [66] J.H. Belo, A.L. Pires, J.P. Araujo, A.M. Pereira, Magnetocaloric materials: from micro- to nanoscale, J. Mater. Res. 34 (2019) 134.