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Towards tailoring the magnetocaloric response in FeRh-based ternary compounds

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In this work, we demonstrate that the magnetocaloric response of FeRh-based compounds may be tailored for potential magnetic refrigeration applications by chemical modification of the FeRh lattice. Alloys of composition $Fe(Rh_{1-x}A_x)$ or $(Fe_{1-x}B_x)Rh$ ($A = Cu$, Pd; $B = Ni$; $0 < x < 0.06$) were synthesized via arc-melting and subsequent annealing in vacuum at 1000 °C for 48 h. The magnetocaloric properties of the FeRh-based systems were determined using isothermal $M(H)$ curves measured in the vicinity of the magnetostructural temperature (T_t). It is found that the FeRh working temperature range (δT_{FWHM}) may be chemically tuned over a wide temperature range, $100\,K \le T \le 400\,K$. While elemental substitution consistently decreases the magnetic entropy change (ΔS_{mag}) of the FeRh-based ternary alloys from that of the parent FeRh compound ($\Delta S_{mag,FeRh} \sim 17$ J/kg K; $\Delta S_{mag,FeRh\text{-}ternary=}$ 7–14 J/kg K at $H_{app} = 2$ T), the net refrigeration capacity (RC), defined as the amount of heat that can be transferred during one magnetic refrigeration cycle, of the modified systems is significantly higher ($RC_{FeRh} \sim 150$ J/kg; $RC_{FeRh\text{-}ternary=}$ 170–210 J/kg at $H_{app} = 2$ T). These results are attributed to stoichiometry-induced changes in the FeRh electronic band structure and beneficial broadening of the magnetostructural transition due to local chemical disorder. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4854975]

In its bulk form, the near-equiatomic phase of $Fe_{1-x}Rh_x$ ($0.47 \le x \le 0.53$) possesses a chemically-ordered B2 (CsCl-type) crystal structure that exhibits an abrupt antiferromagnetic (AFM) to ferromagnetic (FM) phase transition upon heating to $T \sim 350$ K, accompanied by a unit cell volume increase of 1%.[1] In the vicinity of this magnetostructural transition, a giant magnetocaloric effect (MCE)—the phenomenon describing a reversible temperature change upon the application or removal of a magnetic field under adiabatic conditions—has been reported in this compound.[2–4] Direct calorimetry-based measurements of the $Fe_{51}Rh_{49}$ MCE indicate a large adiabatic temperature change $\Delta T_{ad} \sim 13$ K and a magnetic entropy change $\Delta S_{mag} \sim 16$ J/kg K in an external magnetic field change (H_{app}) of 1.95 T.[4] The magnetic refrigeration capacity (RC) (i.e., the amount of heat that can be transferred between the cold and hot reservoirs in one magnetic field cycle) of equiatomic FeRh alloys is reported to be comparable to that of other magnetocaloric compounds such as $Gd_5Ge_2Si_2$ ($\Delta H_{app} = 2$ T provides RCs of FeRh and $Gd_5Ge_2Si_2$ is ~ 130 J/kg and 100 J/kg, respectively).[2,3,5] It is therefore anticipated that despite relatively high raw material and manufacturing costs, the FeRh system may have significant technological potential for incorporation into environmentally-friendly, energy-efficient magnetic cooling devices.[3] From the standpoint of fundamental science, FeRh serves as a test bed for understanding magnetostructural behavior and the associated functional response of intermetallic-based magnetostructural compounds.[6] To date, very little has been reported concerning the magnetocaloric behavior of transition-element-doped FeRh-based systems.[7,8] To fill this knowledge gap, here, the influence of elemental substitution on the magnetocaloric properties of FeRh-based alloys is reported.

Bulk FeRh-based alloys of composition $[Fe(Rh_{1-x}A_x)]$ or $[(Fe_{1-x}B_x)Rh]$ ($A = Cu$, Pd; $B = Ni$; $0 < x < 0.06$) were synthesized by arc melting the constituent elements (99.9% purity) in an Ar atmosphere. The arc-melted ingots were subsequently sealed under vacuum (1×10^{-6} Torr) in vitreous silica tubes for annealing at 1000 °C for 48 h. The chemical composition and homogeneity of the FeRh-based compounds were confirmed by energy-dispersive X-ray spectroscopy in a scanning electron microscope (SEM-EDS, Hitachi S4800), and attainment of the B2-ordered crystal structure was verified using powder X-ray diffraction (PANanalytical X'Pert PRO). Magnetic characterization was carried out using a Vibrating Sample Magnetometer (VSM, Quantum Design model VersaLab) in magnetic fields up to $H = 3$ T and temperatures in the range $50\,K \le T \le 400$ K. The magnetostructural transition temperatures (T_t) of the chemically-modified FeRh alloys were determined from the inflection point of the *M vs. T* transition as the maximum of the derivative of *M* with respect to *T* (*i.e.* $[\frac{\partial M}{\partial T}]_{max}$).[9]

Characteristically, the thermal behavior of magnetocaloric compounds is strongly correlated to the magnetic entropy change (ΔS_{mag}) of the system.[10] The magnetic entropy change (ΔS_{mag}) achieved in the FeRh-ternary compounds was therefore determined from the Maxwell relation using isothermal $M(H)$ curves measured at temperature intervals of 2.5 K in the vicinity of the magnetostructural transition temperature:[10]

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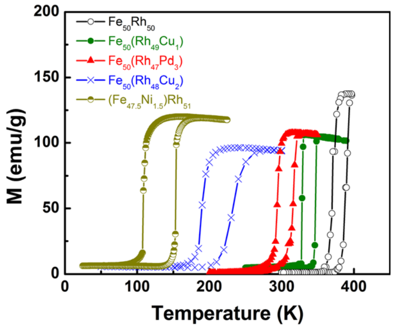

FIG. 1. Temperature-dependant magnetization curves of the 3 d- and 4 d-transition metal substituted FeRh-ternary compounds at an applied magnetic field of $H_{app} = 1$ T.

$$\Delta S_{mag}\left(\frac{T_1 - T_2}{2}\right) = \frac{1}{T_1 - T_2} \times \left[\int_0^{H_{max}} M(T_2, H)dH - \int_0^{H_{max}} M(T_1, H)dH\right]. \tag{1}$$

The area encompassed by the two magnetization curves at temperatures T_1 and T_2 was divided by the temperature difference, $\Delta T = T_2 - T_1$, to determine the ΔS_{mag} at temperature, $T = (T_2 + T_1)/2$. To ensure reproducibility of results, prior to measurement of each $M(H)$ curve, the magnetic history of the sample was reset by cooling the sample down to the antiferromagnetic temperature range ($T = 250$ K for FeRh, Fe$_{50}$(Rh$_{49}$Cu$_1$), and Fe$_{50}$(Rh$_{47}$Pd$_3$); $T = 150$ K for Fe$_{50}$(Rh$_{48}$Cu$_2$); $T = 75$ K for (Fe$_{47.5}$Ni$_{1.5}$)Rh$_{51}$). As per the protocol articulated by Manekar and Roy, the magnetic entropy changes ΔS_{mag} of the samples were calculated using the second magnetization cycle rather than the initial magnetization curve.[2]

The magnetic refrigeration capacity (RC) of the FeRh-based systems at a given applied magnetic field (H_{app}) was estimated from the entropy curves (ΔS_{mag} *vs.* T plot) as

$$RC(H_{app}) = \int_{T_{cold}}^{T_{hot}} \Delta S_{mag}(T, H_{app})dT. \tag{2}$$

Here, the temperatures of the reservoirs, T_{hot} and T_{cold}, correspond to the extreme temperature ends of the full width at half maximum (δT_{FWHM}) of the peak of the ΔS_{mag} *vs.* T curve. The refrigeration cycle in the FeRh system is characteristically accompanied by hysteresis losses that heat the material. The net refrigeration capacity (RC_{net}) was therefore calculated as

$$RC_{net} = RC(H_{app}) - Hysteresis\ Loss.$$

The hysteresis loss was computed from the data using the following equation:

$$Hysteresis\ Loss = \frac{1}{\delta T_{FWHM}} \int_{T_{cold}}^{T_{hot}} \left(\int_0^{H_{max}} M_{desc}(T, H)\, dH - \int_0^{H_{max}} M_{asc}(T, H)\, dH\right) dT, \tag{3}$$

where M_{desc} and M_{asc} represent the ascending and descending field-dependant magnetization curves of the material system.

The equiatomic parent FeRh alloy possesses a saturation magnetization value of ~140 emu/g at $H_{app} = 1$ T and exhibits a first-order AFM → FM phase transition upon heating at ~390 K.[1] (Figure 1).[1] Depending upon the type and concentration of the substituting element, chemical modification of the FeRh lattice decreases both the saturation magnetization (M_s) and the magnetostructural temperature (T_t) relative to that of the equiatomic parent compound while consistently increasing the thermal hysteresis width (ΔT_t) of the magnetostructural transition. Magnetic entropy curves (ΔS_{mag} *vs.* T plots) of the chemically-modified FeRh alloys, shown in Figure 2(a), were constructed from magnetization isotherms measured in the vicinity of the magnetostructural transition. As an example, magnetization isotherms of the Fe$_{50}$(Rh$_{49}$Cu$_1$) sample in the temperature range 325–345 K are shown in Figure 2(b).

The peak magnetic entropy change (ΔS_{mag}^{peak}), δT_{FWHM}, and RC_{net} of the FeRh-ternary alloys are summarized in Table I. It is evident that the ΔS_{mag}^{peak} of the FeRh-based ternary alloys is consistently lower than that of the parent FeRh compound ($\Delta S_{mag,FeRh}^{peak} \sim 17$ J/kg K; $\Delta S_{mag,\,FeRh-X}^{peak} = 7$–$14$ J/kg K at $H_{app} = 2$ T). However, despite high hysteresis losses during the refrigeration cycle, the net refrigeration capacity of the doped FeRh systems is significantly higher than that of equiatomic FeRh system ($RC_{FeRh} \sim 150$ J/kg; $RC_{FeRh\text{-}ternary} = 170$–$210$ J/kg at $H_{app} = 2$ T). As suggested by the theoretical study of Imry and Wortis on the behavior of phase transitions, it is hypothesized that this effect is derived from the presence of microscopic random quenched chemical impurities and local defects.[11] The introduction of small amounts of *3 d*- and *4 d*-transition metal impurities into the FeRh lattice provides a significant amount of chemical disorder, giving rise to a broad transition as compared with that of the equiatomic parent alloy (see Figure 1). From Eq. (2), it follows that the gain in the width of the transition (δT_{FWHM}) can foster a gain in the RC, even though the peak value of the magnetic entropy change is lower than that of the parent alloys. Similar chemical-disorder-induced broadening of the magnetic phase transition has also been observed in other magnetocaloric materials systems such as Gd$_5$Ge$_2$Si$_{x-2}$Fe$_x$[12] and CoMnGe$_{1-x}$Sn$_x$[13] alloys.

Recent work published by the current authors demonstrates that the average weighted valence band electron concentration ($d + s$ electrons) plays an important role in determining the magnetostructural temperature of FeRh-based compounds.[6] Extending this work, the peak magnetic entropy

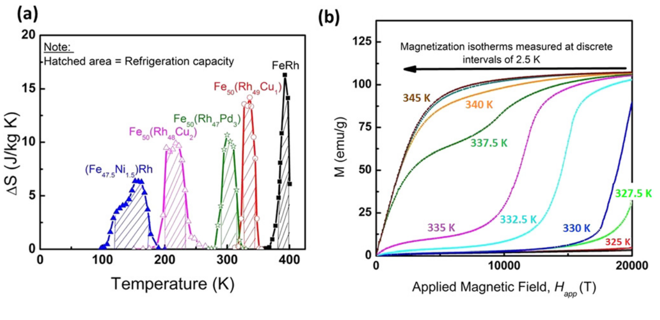

FIG. 2. Magnetic entropy curves (ΔS_{mag} *vs.* T) of the 3 d- and 4 d-transition metal substituted FeRh-ternary compounds at an applied magnetic field of $H_{app} = 2$ T. (b) Magnetization isotherms of the Fe$_{50}$(Rh$_{49}$Cu$_1$) sample in a magnetic field of $H_{app} = 2$ T in the temperature range 325–345 K.

TABLE I. Magnetocaloric properties of the FeRh-based compounds.[a]

			Working temperature range (K)			Refrigeration capacity (J/kg)		
Composition of alloy	Valence electrons per atom	ΔS_{mag}^{peak} (J/kg K)	T_{hot}	T_{cold}	δT_{FWHM}	RC	Hysteresis Loss	RC_{net}
$Fe_{50}Rh_{50}$	8.50	16.37	400	385	15	201	53	148
$Fe_{0.50}(Rh_{0.49}Cu_{0.01})$	8.52	14.40	345	324	21	267	76	191
$Fe_{0.50}(Rh_{0.48}Cu_{0.02})$	8.54	9.91	235	201	34	300	92	208
$Fe_{0.50}(Rh_{0.47}Pd_{0.03})$	8.53	10.68	315	291	24	219	50	169
$(Fe_{0.475}Ni_{0.125})Rh_{0.49}$	8.54	7.37	175	115	60	289	107	182

[a] The magnetocaloric properties reported in this table were measured at an applied magnetic field of $H_{app} = 2\,T$.

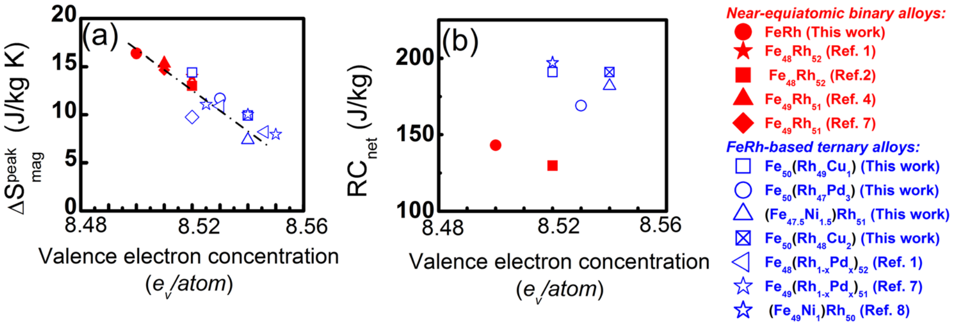

FIG. 3. Dependence of the magnetocaloric properties of FeRh-based ternary compounds on their average weighted valence band electron $((s+d)$ electrons/ atom) concentration: (a) Peak magnetic entropy change (ΔS_{mag}^{peak}) at $H_{app} = 2\,T$ and (b) RC_{net} at $H_{app} = 2\,T$.

change (ΔS_{mag}^{peak}) and the RC_{net} of the FeRh-based compounds synthesized in this study have been plotted as a function of their corresponding valence band concentration in Figure 3. For comparison, ΔS_{mag}^{peak} of FeRh-based compounds previously studied in literature have also been included in Fig. 3(a).[1,2,4,6,7] The linear dependence of the ΔS_{mag}^{peak} values on the valence electron concentration of the chemically-modified FeRh compounds confirms that the magnetic entropy of the FeRh system is strongly influenced by the electronic structure of the system. Further, it may be suggested that the generalized trends noted in the ΔS_{mag}^{peak} *vs.* e_v/atom plot of the FeRh-based ternary alloys provides pathways for predicting the magnetic entropy changes in FeRh alloys over a wide temperature range spanning 100 K–400 K. It follows from Eq. (2) that quantitative assessment of the magnetic RC of FeRh-based ternary compounds requires the capability of predicting the width of the magnetostructural transition width (ΔT_t) of the system. To this end, it is important to realize that though it is known that the ΔT_t of FeRh-based compounds is strongly influenced by the quenched chemical disorder in the system,[14,15] to date no theoretical or empirical study has been conducted to systematically investigate the effect of substitutional doping on the thermal hysteresis width of FeRh-based alloys. It is anticipated that future work to this end would be useful in predicting the net refrigeration capacity of FeRh-based alloys.

In conclusion, in this study the magnetocaloric behavior of FeRh-based systems of composition $Fe(Rh_{1-x}A_x)$ or $(Fe_{1-x}B_x)Rh$ (A = Cu, Pd; B = Ni; $0 < x < 0.06$) was found to vary systematically over a wide temperature range, $100\,K \leq T \leq 400\,K$. Despite a lower peak magnetic entropy change value (ΔS_{mag}^{peak}), the *RC* of the FeRh-based ternary alloys was found to be appreciably higher than that of the parent FeRh compound. While decrease in ΔS_{mag}^{peak} is attributed to changes in the electronic band structure of the FeRh system due to elemental substitution, the enhanced RC in chemically-modified FeRh is ascribed predominantly to local chemical-disorder-induced broadening of the magnetostructural phase transition. Based on previous studies which have shown that the RC of magnetocaloric materials can be enhanced using multiphase materials,[16] it is anticipated that the working temperature range and the magnitude of the refrigeration capacity in the FeRh system may be optimized in a laminated composite of compositionally-tuned $(Fe(Rh_{1-x}M_x)$ or $(Fe_{1-x}M_x)Rh$ components, where $0.48 \leq x \leq 0.52$ and $M = 3d$ or $4d$ transition element). While the thermal hysteresis effect found in the FeRh system may reduce the magnitude of the MCE, possible optimal cooling cycles have been suggested in the literature.[17,18] These results highlight correlations between the valence band electron concentration and the magnetic entropy change of $3d$- and $4d$-substituted FeRh compounds, allowing prediction of the magnetic entropy changes in this system.

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