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MnAs and MnFeP\(_{1-x}\)As\(_x\)-based magnetic refrigerants: a review

Ume e Habiba\(^1\), Khurram Shehzad Khattak\(^{2,4}\), Shahid Ali\(^1\) and Zawar Hussain Khan\(^3\)

\(^1\) Materials Research Laboratory, Department of Physics, University of Peshawar, Peshawar, 25120, Pakistan
\(^2\) Department of Computer Systems Engineering, University of Engineering and Technology, Peshawar, 25120, Pakistan
\(^3\) Department of Electrical Engineering, University of Engineering and Technology, Peshawar, 25120, Pakistan

E-mail: ume.habiba15@yahoo.com, khurram.s.khattak@uetpeshawar.edu.pk, drshahidali@uop.edu.pk and zawarkhan@nwfpuet.edu.pk

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Abstract

This paper presents a comparative analysis of MnAs and MnFeP\(_{1-x}\)As\(_x\) family and its alloys from magnetic refrigeration perspective. A thorough literature review was undertaken and to the best of authors knowledge, all samples (~100 samples) with their Curie temperature (\(T_c\)) in the range 260–340 K have been reported. For contrastive analysis, samples have been grouped based on their structural and experimental conditions such as magnetic field and sample composition etc. For comparative analysis, all variables of magnetocaloric effect (MCE), e.g., \(T_c\), magnetic entropy change (\(\Delta S_m\)), adiabatic temperature change (\(\Delta T_{ad}\)) and relative cooling power (RCP) have been considered with calculated missing variables, wherever possible. The first objective of this paper was to perform a comparative analysis of different fabrication variables (e.g., particle size, shape, morphology, chemical composition, structure, purity of starting materials, homogeneity, annealing, and synthesis methods) on the overall MCE properties of the aforementioned family. In addition, the best fabrication practices for further improvement in MCE properties are proposed. The second objective was to observe different material’s doping (e.g., Cr, Si, Ge, B) in hysteresis loss mitigation and MCE properties enhancement. Best doping materials were suggested for the compositions, which were displaying optimum MCE properties for further MCE enhancement. Lastly, but most importantly, to propose a high performing magnetic refrigerant by: (1) shortlisting a composition with optimum MCE properties; (2) further enhancement in MCE through adopting best fabrication processes for the said magnetic refrigerant; (3) suggesting best doping material for hysteresis loss mitigation and MCE enhancement; and most importantly (4) fabricating the proposed magnetic refrigerant as a nanostructure; thus, improving MCE properties through broadening of \(T_c\) curve.

1. Introduction

The existence of MCE has been known for over 100 years, interest in its physics and applications in magnetic refrigeration has been growing at a rapid pace due to increasing concerns about energy efficiency and environment [1–5]. An ideal material for magnetic refrigeration should be composed of relatively inexpensive raw materials, have a high MCE and have a little or no irreversible hysteresis losses [6–8]. For a large MCE to exist, there must be a large change in \(\Delta S_m\) over a small temperature range. Families exhibiting giant magnetocaloric effect (GMCE) can be attributed to a first-order phase transition (FOPT) in combination with magnetic ordering and electronic band structure changes [9–11]. High performing families such as La(Fe\(_x\)Si\(_{1-x}\))\(_3\) and Gd\(_2\)(Si\(_x\)Ge\(_{1-x}\))\(_3\), exhibiting much higher \(\Delta S_m\), undergo structural transition in combination with magnetic ordering and electronic band structure changes in addition to magnetic transition [12–14].

Instead of searching for new magnetic refrigerants, a working magnetic refrigerant can be fabricated from one of the well-established high performing families such as MnAs and MnFeP\(_{1-x}\)As\(_x\) [14–18] by: (1) shortlisting...
best performing composition with Tc between 260–340 K; (2) MCE enhancement through adopting best fabrication processes (e.g., particle size, shape, morphology, chemical composition, structure, purity of starting materials, homogeneity, annealing and synthesis methods) for the said composition; (3) MCE enhancement by using best doping material for hysteresis mitigation; and (4) fabricating the said composition as nanostructure (3–50nm, depending upon composition), thus, further improving MCE properties through broadening of the Tc curve [13]. An example is of MnAs0.97P0.03 where hysteresis was reduced by 60% from 10 K at Tc for an annealed sample with a mean size of 23 nm to 2 K for as-milled sample with a mean size of 100 nm.

1.1. MnAs alloys

MnAs is a ferromagnetic with hexagonal NiAs-type crystal structure below its Tc at 318 K, which changes to paramagnetic with orthorhombic MnP-type structure [9, 14, 15, 19–22]. At about 378 K, it undergoes SOPT, changing again from Mn-P type to NiAs type, with MnP-type structure stable only in the thermal range of 318–378 K [20, 23]. MnAs with magnetization saturation of 3.4 μB/Mn exhibits ∆SM and ∆Tad as large as 30 J/kg K and ~13 K, under a magnetic field (H) of 5 T, as can be seen in table 1 [19].

The entropic magnetic limit for MCE in MnAs is given by ∆SM = R ln (2J + 1) = 103 J/kg K, where R is the gas constant and J is the total angular momentum of the magnetic ion, assuming magnetic field independence of lattice and electronic entropy contributions [20, 21, 41]. Using Maxwell relation to calculate ∆SM as a function of ΔH works seamlessly for second-order phase transition (SOPT) but results in big errors for FOPT due to thermal hysteresis and discontinuity in magnetization, often resulting into a ‘spike’ at Tc, as reported for MnAs [9, 19, 40]. Bratko et al [31] preferred calorimeters for MCE measurement instead of the indirect approach involving isothermal magnetization measurements and the Maxwell relation to counter spurious results. Through careful use of the Maxwell relation and Clausius-Clapeyron equation a more realistic MCE estimations can be achieved. For example, Mn0.99 Fe0.01 As where ∆SM with and without Clausius-Clapeyron equation is 26 J/kg K [32] and 325 J/kg K [33] respectively as can be seen in table 1. Second example of aforementioned phenomena is ∆SM of Mn0.995 Pr0.005 As, which was 30.2 J/kg K instead of 135 J/kg K after using the Clausius-Clapeyron equation [39]. When a system undergoes a first-order transformation, the entropy of the system as a function of temperature exhibits a discontinuity related to the entropy transformation Str. On the other hand, application of a magnetic field promotes a shift in the transformation temperature expressed by the Clausius-Clapeyron equation. If the effect of the magnetic field is large enough to cause transformation of the first order, but its effect on the heat capacities of the two phases is low, it should be assumed that the limit value of the MCE with ∆S ∼ ∆S0 should be as high as possible. The isothermal entropy change ∆S caused by the applied magnetic field is obtained by numerical integration of the Maxwell relation from isothermal magnetization curves M(H)/T. In the case of magnetostuctural transitions of first-order, this procedure was controversial because of the existence of transformation hysteresis. It is now known that the use of Maxwells relation for the first order system in the vicinity of the Curie temperature is not true if the experimental data are typically obtained in nonequilibrium condition as a result of metamagnetic transition.

The magnetization and magnetic domains of ferromagnetic MnAs nanocounters (NCs) located at a relatively close range in a bended MnAs / InAs heterojunction nanowire (NW), sometimes observed in NWs with multiple MnAs NCs, based on the structural and magnetization characterization results. In particular, in the case of MnAs NCs formed in the nearly straight (or slightly bending) NWs, the magnetization of MnAs NCs was oriented along the external magnetic field directions. Nevertheless, magnetic force microscopy tip magnetization sometimes guided the magnetization of a MnAs NC at the distinctly bending position of heterojunction NWs. The decrease in NC coercion may have played an important role in switching magnetization directions in the NCs at the heterojunction NW’s bending position [42].

MnAs present high MCE properties under hydrostatic pressure, which is absent in other well-known families such as Gd2Ge2Si2 [12, 43]. Effects of hydrostatic pressure on MnAs were studied concluding: (1) Tc decreases as pressure increase, and (2) directly proportional exponential increase in MCE with pressure, culminating at ∆SM of 267 J/kg K for 2.23 kbar after which the effect starts diminishing and becoming deleterious after 2.64 kbar [21]. Wada et al [25] also studied the effect of pressure by noting an improvement in MCE of MnAs with ∆SM = 36 J/kg K at 2.09 kbar and ∆SM = 30 J/kg K for MnAs0.93 Sb0.07 at 3.37 kbar. The deleterious effect after a certain pressure was due to the broadening of magnetic transition under high pressure [21, 25].

Importance of purity of the starting materials has already been established in literature [13, 21, 44]. This is further validated by comparing experimental data of eight different MnAs samples, as reported in table 1. The highest ∆SM of 47 J/kg K is because of starting material’s purity (prepared with Mn = 99.999% and As = 99.9999% purity) [21]. Effect of starting material’s purity on MnAs MCE curve can be seen graphically in figure 1. A direct relation between composition’s heterogeneity, grain size, synthesis, defects, thermal hysteresis and a narrow interval for the transition around the Tc values had been established [9, 13]. In this regard, 'Shock
| Sample            | $T_c$ (K) | $|\Delta S_m|$ (J/kgK) | $\Delta T_{ad}$ (K) | $\Delta H$ (kOe) | RCP (J/Kg) | $\Delta T_{hys}$ (K) | References |
|-------------------|-----------|-------------------------|---------------------|------------------|------------|----------------------|------------|
| MnAs              | 318       | 47                      | 50                  | 50               |            |                      |            |
|                   | 281       | 267                     | 50                  |                  |            |                      |            |
|                   | 326       | 21.96                   | 50                  | 5–10             |            |                      |            |
|                   | 305       | 29.3                    | 10.27               | 755              |            |                      |            |
|                   | 318       | 41                      | 13                  | 5                |            |                      |            |
|                   | 311       | 15                      | 100                 |                  |            |                      |            |
|                   | 285$^a$   | 36                      | 20                  | 6                |            |                      |            |
|                   | 318$^a$   | 31                      | 20                  | 124$^a$          |            |                      |            |
|                   | 318$^a$   | 38$^a$                  | 50                  | 418$^a$          |            |                      |            |
| MnP               | 290       | 2.2                     | 10                  |                  |            |                      |            |
|                   |           | 3.3                     | 20                  |                  |            |                      |            |
|                   |           | 6                       | 50                  |                  |            |                      |            |
| MnAs$_{0.99}$P$_{0.01}$ | 301$^a$ | 40                      | 13                  | 140              |            |                      |            |
| MnAs$_{0.98}$P$_{0.02}$ | 296$^a$ | 50                      | 15                  | 140              | 400$^a$   |                      |            |
| MnAs$_{0.97}$P$_{0.03}$ | 275     | 14                      | 50                  | 294$^a$          |            |                      |            |
| Fe$_{0.8}$Mn$_{1.5}$As | 287.5  | 6.2                     | 50                  | 92$^a$           |            |                      |            |
| Mn$_{0.99}$Fe$_{0.01}$As | 295     | 16.4                    | 80                  | 300$^a$          |            |                      |            |
| Mn$_{0.99}$Fe$_{0.01}$As | 294     | 26                      | 20                  |                  |            |                      |            |
| Mn$_{0.99}$Fe$_{0.01}$As | 289     | 29.3                    | 50                  |                  |            |                      |            |
| Mn$_{0.99}$Fe$_{0.01}$As | 272$^a$ | 90$^a$                  | 50                  |                  |            |                      |            |
Table 1. (Continued.)

| Sample                  | $T_c$ (K) | $|\Delta S_{ad}|$ (J/kgK) | $\Delta T_{ad}$ (K) | $\Delta H$ (kJ/Kg) | RCP (J/Kg) | $\Delta T_{hys}$ (K) | References |
|-------------------------|-----------|-----------------------------|---------------------|-------------------|------------|----------------------|------------|
| Mn$_{0.9875}$Fe$_{0.0125}$As  | 286$^a$   | 275$^a$                      |                     |                   |            |                      |            |
| Mn$_{0.99}$Fe$_{0.01}$As      | 295$^a$   | 325$^a$                      |                     |                   |            |                      |            |
| Mn$_{0.9285}$Fe$_{0.0175}$As  | 272$^a$   | 90$^a$                       |                     |                   |            |                      |            |
| Mn$_{0.9875}$Fe$_{0.0125}$As  | 286$^a$   | 275$^a$                      |                     |                   |            |                      |            |
| Mn$_{0.99}$Fe$_{0.01}$As      | 295$^a$   | 325$^a$                      |                     |                   |            |                      |            |
| Mn$_{0.994}$Fe$_{0.006}$As    | 310$^a$   | 240$^a$                      |                     |                   |            |                      | [33]       |
| Mn$_{0.997}$Fe$_{0.003}$As    | 310$^a$   | 330$^a$                      |                     |                   |            |                      |            |
| Mn$_{0.94}$Cu$_{0.06}$As      | 308.3     | 21                           |                     |                   |            |                      | [23]       |
| Mn$_{0.97}$Cu$_{0.03}$As      | 317$^a$   | 174$^a$                      |                     |                   |            |                      | [34]       |
| Mn$_{0.94}$Cu$_{0.06}$As      | 316$^a$   | 159$^a$                      |                     |                   |            |                      |            |
| Mn$_{0.97}$Cu$_{0.03}$As      | 317$^a$   | 164$^a$                      |                     |                   |            |                      | [20]       |
| MnAs$_{0.9}$Sb$_{0.1}$        | 280       | 30                           |                     |                   |            |                      |            |
| MnAs$_{0.95}$Sb$_{0.05}$     | 310$^a$   | 31$^a$                       |                     |                   |            |                      | [35]       |
| MnAs$_{0.97}$Sb$_{0.03}$     | 295$^a$   | 10.2$^a$                     |                     |                   |            |                      |            |
| MnAs$_{0.93}$Sb$_{0.07}$     | 308$^a$   | 14$^a$                       |                     |                   |            |                      |            |
| MnAs$_{0.97}$Sb$_{0.03}$     | 305$^a$   | 27.5$^a$                     |                     |                   |            |                      |            |
Table 1. (Continued.)

| Sample                  | $T_1$ (K) | $|ΔS_m|_m$ (J/kgK) | $ΔT_{ad}$ (K) | $ΔH$ (kOe) | RCP (J/Kg) | $ΔT_hys$ (K) | References |
|-------------------------|-----------|------------------|--------------|------------|-----------|--------------|------------|
| MnAs$_{0.927}$ Sb$_{0.073}$ | 310$^a$  | 11$^a$          | 10           |            | 33$^a$    |              |            |
| MnAs$_{0.93}$ Sb$_{0.07}$  | 273$^a$  | 30$^a$          | 20           |            | 260$^a$   |              |            |
| Mn$_{0.9875}$ Cr$_{0.0125}$ As | 315$^a$  | 38               | 15$^a$       | 50         | 893       | 12.3         | [35]       |
| Mn$_{0.9875}$ Cr$_{0.0065}$ Fe$_{0.006}$ As | 287$^a$  | 42               | 13.5$^a$     | 50         | 730       | 13.7         |            |
| Mn$_{0.994}$ Cr$_{0.006}$ As | 292       | 13.7            | 50           |            | \(\ldots\) | 5            | [37]       |
| Mn$_{0.9}$ Cr$_{0.1}$ As | 267       | 20.2            | 50           |            | 283$^b$   | 10–30        |            |
| MnAs$_{0.94}$ Si$_{0.06}$ N | 263       | 12.8            | 50           |            | 319       |              | [38]       |
| MnAs$_{0.91}$ Si$_{0.09}$ N | 285       | 10.6            | 50           |            | 274       | 0            |            |
| Mn$_{0.99}$ Pr$_{0.005}$ As | 318       | 30.2            | 50           |            | 20        |              | [39]       |
| Mn$_{0.99}$ Pr$_{0.01}$ As | 320       | 27.9            | 50           |            |           |              |            |
| Mn$_{0.99}$ Pr$_{0.01}$ As | 321       | 25.2            | 50           |            |           |              |            |
| Mn$_{0.99}$ Pr$_{0.02}$ As | 320       | 23.3            | 50           |            |           |              |            |
| Mn$_{0.99}$ Co$_{0.01}$ As | 316       | 32.1            | 17.7         | 60         |           |              | [40]       |
| Mn$_{0.9}$ Ti$_{0.05}$ V$_{0.05}$ As | 266       | 30              | 20           |            | 120$^c$   |              | [26]       |
| Mn$_{0.9}$ Ti$_{0.05}$ V$_{0.05}$ As | 266$^c$ | 36$^c$         | 50           |            | 250$^c$   |              |            |

$^a$ Approximation from the figures in the cited papers.

$^b$ Calculated from the figures in the cited papers.
compaction' although making manufacturing process more efficient, affect MCE deleteriously because of compositional heterogeneity. An example is MnAs$_1$Sb$_x$ ($x = 0.068, 0.073$) before and after shock compaction, as can be seen in table 1 [35]. Paganotti et al [45] reported in their work that the thermal hysteresis is independent of the formed phase fraction. In a temperature interval around the magnetic transition temperature, the study was conducted using a differential scanning calorimeter and different heating rates. The experiment consisted of two procedures, the first of which analyzed at different heating rates the onset and peak temperatures of the thermal event associated with the magnetic transition. The second procedure consisted of studying the formation and decomposition of the process associated with the magnetic transition as a function of the temperature by means of thermal event enthalpy. The results showed that the onset temperatures during cooling increased almost linearly with cooling rate and the onset temperatures during heating are almost constant. In addition, the transition enthalpy varied with heating rate and progress of reaction, showed various behaviors during heating and cooling, indicated two different mechanisms for the transition phase.

Large thermal and magnetic hysteresis dependence upon composition and magnetic field is a major drawback for MnAs family [25, 31, 37]. A lot of effort has gone into hysteresis mitigation and MCE enhancement through doping/substitution of different materials such as S, Se, Te, Bi, and P with unsatisfactory results because of low solubility with MnAs. Substitution of Fe and Cu for Mn resulted in better MCE because of their solubility, smaller atomic radii and external pressure effect emulation [34, 41, 46]. Doping of Sb, Cr and interstitial N have a positive effect on hysteresis reduction. Substitution of small amount of Sb for As can be used to lower $T_c$ and more importantly thermal hysteresis to about 1 K, while maintaining NiAs-type structure and FOPT [20, 25, 32]. The interstitial nitrogen results in an increase in $T_c$ and slight enhancement of MCE, while Si results in $T_c$ decrease [38]. Thermal and magnetic hysteresis are both reduced to nearly zero with the silicon content in MnAs$_{1-x}$Si$_x$N$_x$. On the downside, Si, Sb and N doped materials though reducing hysteresis does not show marked improvement in MCE properties for this family, as can be observed in table 1. The reduction in $T_c$ for T (Co, Ni and Cu) content is independent of the transition metal species and independent of the position they occupy [Fe(3f)/Mn(3g)], suggesting that the ferromagnetic FM interaction with transition metal substitution is weakened. However, the slopes of the curves are different. $T_c$ is most sensitive to Cu substitution and least sensitive to Co substitution. As for the same transition metal replacement at different sites, when a transition metal is replaced by Fe, $T_c$ is more sensitive than Mn. This can be easily understood with mixed magnetism, since the reconstruction of electron density leads to the first-order phase transition in Fe$_2$P-based (Mn, Fe)$_2$P$_2$Si compounds in the bond between Fe and P/Si. In addition, we found that with increasing T (Co, Ni and Cu) content, the lattice parameter ratio $c/a$ increases. It is known that the interaction between the nearest 3f–3g inter-layer is responsible for FM ordering in Mn–Fe–P–Si compounds and is more sensitive to changes in the $c/a$ ratio than to the parameters $a$ and $c$ in the lattice itself, resulting in a linear relationship between $T_c$ and the $c/a$ ratio. However, substitution alters not only the interatomic distances but also the electron density, which is a key factor in Fe$_2$P-based compounds [47].

Substitution of Mn by Cr reduces (or even eliminates depending upon substitution) both $T_c$ and thermal hysteresis while having positive effect on overall MCE [29, 36, 37]. An example is thermal hysteresis elimination in Mn$_{0.994}$Cr$_{0.006}$As and its reduction to ~5 K in Mn$_{0.99}$Cr$_{0.01}$As [4]. The Fe substitution in the Mn$_{0.9875}$
Cr$_{0.0065}$ Fe$_{0.006}$ As compound results in an increase and decrease in thermal hysteresis and RCP, respectively, as compared to the Mn$_{0.9875}$ Cr$_{0.0125}$ As; however, high values of $|\Delta S|_{ad}$ are still obtained [36].

Mn$_{0.9875}$ Cr$_{0.0125}$ As and Mn$_{0.9875}$ Cr$_{0.0065}$ Fe$_{0.006}$ As are thus the best performing composition in this family exhibiting highest RCP, $\Delta T_{ad}$ and $|\Delta S|_{ad}$ values with lowest hysteresis. Furthermore, Mn$_{0.99}$ Co$_{0.01}$ As is also of interest as it possess the highest reported $\Delta T_{ad}$. It is therefore proposed that from MnAs and its alloys, these should be synthesized as nanostructures with high purity starting materials to achieve a further improvement in MCE of at least 40% [13, 48].

1.2. MnFe(P, As) Alloys

The poisonous nature of As has compelled to develop arsenic-free alloys with the same outstanding MCE properties. MnFeP$_{1-x}$As$_x$ crystalllographic structure and physical properties are strongly influenced by the relative atomic size, valence-electron concentrations and are highly sensitive to P/As ratio [49–53]. These alloys with Fe$_2$P-type structure not only exhibit excellent MCE properties around room temperature but also have a tailorable $T_c$ as a function of $x$ and inexpensive constituents as compared to rare-earth containing materials [54].

In the intermediate 0.15 $< x < 0.65$ composition range, the compounds crystallize in the Fe$_2$P-type structure and the magnetic moments of the Mn and Fe atoms order ferromagnetically, with $T_c$ increasing with $x$ up to 332 K for $x = 0.65$ [50].

Besides toxicity of As, thermal hysteresis (~15–22 K) inherent of FOPT is another major drawback for this family [55, 56]. On the first account, As was replaced with Si and/or Ge exhibiting promising results, as can be seen in table 2. Substitution of Si results in an increase in $T_c$ and MCE properties while also increasing thermal hysteresis on the downside [50, 57, 58]. For MnFeP$_{1-x}$Si$_x$ compounds, a hexagonal Fe$_2$P-type structure was observed for 0.28 $< x < 0.64$ with a very large $|\Delta S|_{ad}$ of 30 J/kgK for MnFeP$_{0.5}$ Si$_{0.5}$ accompanied by a large thermal hysteresis (above 20 K) [52].

Thermal hysteresis mitigation while maintaining large MCE properties can be achieved by varying P:Si ratio and keeping high Mn ratio, such as Mn$_{1.4}$ Fe$_{0.6}$ Si$_{0.5}$ P$_{0.5}$ with virtually no thermal hysteresis [58]. The same can also be accomplished by increasing Mn:Fe ratio with reported thermal hysteresis to less than 1 K [61].

Mn$_{1.2}$ Fe$_{0.8}$ P$_{1-x}$Si$_x$B$_{0.05}$ is a prime example, where a stepwise thermal hysteresis of 10, 8 and 0.4 is obtained for $x = 0.4, 0.5$ and 0.55, respectively [63]. Ni substitutions reduces thermal hysteresis while Cu substitution increases it. Co substitution for Mn reduces thermal hysteresis while when substituted for Fe, results in hardly any change, although it has displayed highest $|\Delta S|_{ad}$ for MnFePSi alloys, as can be seen in table 2 [47]. On the other hand, substitution of Ru/Ni for Fe in (Mn, Fe)$_2$PSi was effective in thermal hysteresis reduction to less than 2 K [62, 71]. FOPT and thus high MCE properties for (Mn, Fe)$_2$(P, Si) alloys can be preserved by; i) tuning Mn/Fe and P/Si ratios, ii) performing varied heat treatment and/or iii) introducing doping atoms such as B, C and N exhibiting different effects on thermal/magnetic hysteresis and magnetic interactions [47].

Ge-substituted compounds retain Fe$_2$P-type crystal structure, but reorientation of lattice parameter leads to changes in inter-atomic distances and exchange interactions between Mn-Mn, Fe-Fe, and Mn-Fe ions. This results in an increase in $T_c$, linearly proportional to Ge contents and with magnetic transition becoming second-order [54, 64, 70]. Although hysteretic behavior is characteristic of FOPT, in MnFe(P, Ge) it can be reduced by changing Mn/Fe ratio, as shown for bulk samples of Mn$_{2-y}$Fe$_y$P$_{0.75}$Ge$_{0.25}$ ($y = 0.84, 0.82, 0.80, 0.74$) [64].
Table 2. All compositions of MnFe(P, As) and its alloys as reported in literature with Curie Temperature in the range of 260–340 K.

| Sample          | T<sub>c</sub> (K) | |ΔS<sub>0</sub>| (J/kgK) | ΔT<sub>ad</sub>(K) | ΔH (kOe) | RCP (J/Kg) | ΔT<sub>hys</sub>(K) | References |
|-----------------|-------------------|-----------------|------------------|-------------------|-----------------|-------------------|-------------------|-------------------|------------|
| MnFeP<sub>0.5</sub> As<sub>0.5</sub> | 282               | 18<sup>a</sup> | 30               | 252<sup>b</sup>   |               |                   |                   | [59]              |
|                 | 282<sup>c</sup>   | 18              | 50               | 290<sup>b</sup>   |               |                   |                   | [51]              |
|                 | 282 <sup>c</sup>  | 16              | 30               | 256<sup>b</sup>   |               | 20                |                   | [57]              |
| MnFeP<sub>0.45</sub> As<sub>0.55</sub> | 303               | 18<sup>c</sup> | 6<sup>c</sup>   | 50                |               |                   |                   | [53]              |
| MnFeP<sub>0.45</sub> As<sub>0.55</sub> | 306               | 14              | 4                | 20                |               |                   |                   | [14]              |
| MnFeP<sub>0.47</sub> As<sub>0.53</sub> | 296               | 12.5            | 3.4              | 20                |               |                   |                   |                   | [14]              |
| Mn<sub>1.1</sub>Fe<sub>0.9</sub>P<sub>0.5</sub> As<sub>0.5</sub> | 264<sup>c</sup>   | 21.5            | 50               | 300<sup>b</sup>   |               |                   |                   | [51]              |
| Mn<sub>1.1</sub>Fe<sub>0.9</sub>P<sub>0.47</sub> As<sub>0.53</sub> | 292               | 21              | 4.2              | 20                |               |                   |                   | [14]              |
| MnFeP<sub>0.5</sub> Si<sub>0.5</sub> | 299               | 0.5             |                   |                   |               |                   |                   | [50]              |
| MnFeP<sub>0.5</sub> Si<sub>0.4</sub> | 303               | 30              | 240<sup>b</sup>  |                   |               |                   |                   | [57]              |
| MnFeP<sub>0.5</sub> Si<sub>0.3</sub> | 294               | 32              | 30               | 192<sup>a</sup>   |               |                   |                   |                   | [53]              |
| MnFeP<sub>0.5</sub> Si<sub>0.2</sub> | 280               | 21              | 30               | 210<sup>b</sup>   |               |                   |                   |                   | [52]              |
| MnFeP<sub>0.5</sub> Si<sub>0.1</sub> | 268               | 10              | 20               |                   |               | 21                |                   |                   | [52]              |
| MnFeP<sub>0.5</sub> Si<sub>0.5</sub> | 332               | 30              | 20               | 150<sup>b</sup>   |               | 23                |                   |                   | [52]              |
Table 2. (Continued.)

| Sample | $T_c$ (K) | $|\Delta S_f|$ (J/kgK) | $\Delta T_{ad}$ (K) | $\Delta H$ (kJOe) | RCP (J/Kg) | $\Delta T_{hys}$ (K) | References |
|--------|-----------|---------------------|-----------------|-----------------|-------------|-------------------|------------|
| Mn$_{1.20}$Fe$_{0.75}$P$_{0.50}$Si$_{0.50}$ | 299 | 26° | 20 | 260° | | | [61] |
| Mn$_{1.22}$Fe$_{0.7}$P$_{0.50}$Si$_{0.50}$ | 285° | 22° | 20 | 176° | | | |
| Mn$_{1.20}$Fe$_{0.65}$P$_{0.50}$Si$_{0.50}$ | 268° | 15° | 20 | 90° | | | |
| Mn$_{1.24}$Fe$_{0.6}$Si$_{0.5}$P$_{0.5}$ | 332 | 28.6 | 50 | | | | [58] |
| Mn$_{1.24}$Fe$_{0.6}$Si$_{0.5}$P$_{0.5}$ | 302 | 22.9 | 50 | | | | |
| Mn$_{1.24}$Fe$_{0.6}$Si$_{0.5}$P$_{0.5}$ | 267 | 14.5 | 50 | | | | |
| Mn$_{1.24}$Fe$_{0.4}$P$_{0.5}$Si$_{0.5}$ | 320° | 13° | 20 | 78° | | < 2.5 | [62] |
| Mn$_{1.24}$Fe$_{0.5}$Ru$_{0.15}$P$_{0.5}$Si$_{0.5}$ | 290° | 15° | 20 | 35° | | | |
| Mn$_{1.24}$Fe$_{0.7}$Ru$_{0.1}$P$_{0.5}$Si$_{0.5}$ | 272° | 13° | 20 | 65° | | | |
| Mn$_{1.24}$Fe$_{0.73}$Ru$_{0.05}$P$_{0.5}$Si$_{0.5}$ | 305° | 11° | 20 | 100° | | | |
| Mn$_{1.24}$Fe$_{0.7}$Ni$_{0.10}$P$_{0.5}$Si$_{0.5}$ | 270° | 12° | 20 | | | | [62] |
Table 2. (Continued.)

| Sample          | $T_c$ (K) | $|\Delta S_v|$ (J/kgK) | $\Delta T_{ad}$ (K) | $\Delta H$ (kOe) | RCP (J/Kg) | $\Delta T_{hys}$ (K) | References |
|-----------------|-----------|------------------------|---------------------|------------------|------------|----------------------|------------|
| Mn$_{1.2}$Fe$_{0.75}$Ni$_{0.02}$P$_{0.5}$Si$_{0.5}$ | 300$^a$ | 8$^a$ | 20 | | | | [47] |
| Mn$_{1.2}$Fe$_{0.74}$Ni$_{0.01}$P$_{0.5}$Si$_{0.5}$ | 310$^b$ | 8$^b$ | 20 | | | | [47] |
| Mn$_{0.8}$Co$_{0.16}$P$_{0.5}$Si$_{0.5}$ | 281$^b$ | 30$^b$ | 50 | 300$^b$ | | <1 | [47] |
| Mn$_{0.9}$Co$_{0.2}$Fe$_{0.95}$P$_{0.5}$Si$_{0.5}$ | 325$^b$ | 19$^b$ | 50 | 380$^b$ | | | [47] |
| Mn$_{1.2}$Fe$_{0.8}$P$_{0.45}$Si$_{0.55}$B$_{0.05}$ | 280 | 11.1 | 50 | 270 | | 0.8 | [63] |
| MnFeP$_{0.67}$Si$_{0.22}$Ge$_{0.11}$ | 270 | 14 | 50 | 266$^b$ | | | [55] |
| MnFeP$_{0.45}$Si$_{0.26}$Ge$_{0.11}$ | 292 | 16 | 50 | 384$^b$ | | | [55] |
| MnFeP$_{0.38}$Si$_{0.3}$Ge$_{0.11}$ | 288 | 14 | 50 | 238$^b$ | | | [55] |
| MnFeP$_{0.36}$Si$_{0.33}$Ge$_{0.11}$ | 260 | 13 | 50 | 221$^b$ | | | [55] |
| MnFeP$_{0.3}$As$_{0.44}$Ge$_{0.06}$ | 312$^b$ | 11.5$^a$ | 30 | 207$^b$ | | | [59] |
| MnFeP$_{0.3}$As$_{0.78}$Ge$_{0.22}$ | 280 | 38$^b$ | 50 | 760$^b$ | | | [54] |
Table 2. (Continued.)

| Sample         | \( T_\text{c} \) (K) | \(|\Delta S_\text{c}\)| (J/kgK) | \( \Delta T_{\text{ad}} \) (K) | \( \Delta H \) (kOe) | RCP (J/Kg) | \( \Delta T_{\text{hys}} \) (K) | References |
|----------------|------------------|----------------|----------------|----------------|-------------|----------------|-------------|
| MnFeP<sub>0.9</sub>As<sub>0.77</sub>Ge<sub>0.23</sub> | 309<sup>a</sup> 31<sup>b</sup> | 50 465<sup>b</sup> | | | | | |
| MnFe<sub>0.9</sub>P<sub>0.81</sub>Ge<sub>0.19</sub> | 260              | 13.8          | 20            | 276<sup>b</sup> | [64]        | | | |
| MnFe<sub>0.9</sub>P<sub>0.78</sub>Ge<sub>0.22</sub> | 296              | 20            | 20            | 200<sup>b</sup> | | | | |
| MnFe<sub>0.9</sub>P<sub>0.75</sub>Ge<sub>0.25</sub> | 330              | 13            | 20            | 117<sup>b</sup> | | | | |
| MnFe<sub>0.9</sub>P<sub>0.75</sub>Ge<sub>0.25</sub> | 320              | 24.5          | 20            | …             | | | | |
| Mn<sub>1.2</sub>Fe<sub>0.8</sub>P<sub>0.75</sub>Ge<sub>0.25</sub> | 288              | 20.3          | 20            | 151           | | | | |
| Mn<sub>1.22</sub>Fe<sub>0.78</sub>P<sub>0.72</sub>Ge<sub>0.25</sub> | 274              | 15.3          | 20            | 162           | | | | |
| Mn<sub>1.1</sub>Fe<sub>0.9</sub>P<sub>0.81</sub>Ge<sub>0.19</sub> | 260              | 14            | 6             | 20            | 115<sup>b</sup> | | | | 65
| Mn<sub>1.1</sub>Fe<sub>0.8</sub>P<sub>0.78</sub>Ge<sub>0.22</sub> | 298              | 20            | 4             | 20            | 160<sup>b</sup> | | | | |
| Mn<sub>1.1</sub>Fe<sub>0.9</sub>P<sub>0.75</sub>Ge<sub>0.25</sub> | 330              | 13            | 2             | 20            | 130<sup>b</sup> | | | | |
| Mn<sub>1.1</sub>Fe<sub>0.9</sub>P<sub>0.8</sub>Ge<sub>0.2</sub> | 267.5            | 29            | 20            | 75<sup>b</sup> | 9-16        | | | | | 66
| Mn<sub>1.1</sub>Fe<sub>0.9</sub>P<sub>0.78</sub>Ge<sub>0.24</sub> | 280<sup>a</sup> 46.5 | 50 558<sup>b</sup> | | | | | | |
| Sample                      | $T_c$ (K) | $|\Delta S_m|$ (J/kgK) | $\Delta T_{ad}$ (K) | $\Delta H$ (kJOe) | RCP (J/kg)   | $\Delta T_{hys}$ (K) | References |
|-----------------------------|-----------|------------------------|---------------------|------------------|--------------|------------------------|------------|
| Mn$_{1.1}$Fe$_{0.9}$P$_{0.7}$Ge$_{0.24}$ (Ribbon) | 317       | 35.4                   | 50                  | 496$^b$          |              |                        | [56]       |
| Mn$_{1.1}$Fe$_{0.9}$P$_{0.7}$Ge$_{0.24}$ (Bulk) | 299       | 26.1                   | 50                  | 522$^a$          |              |                        |            |
| Mn$_{1.2}$Fe$_{0.8}$P$_{0.7}$Ge$_{0.26}$ | 337$^c$   | 44.9                   | 50                  | $\sim$10         |              |                        | [68]       |
| Mn$_{1.2}$Fe$_{0.8}$P$_{0.7}$Ge$_{0.24}$ | 298       | 11.7                   | 20                  | 175$^b$          |              |                        | [69]       |
| Mn$_{1.2}$Fe$_{0.8}$P$_{0.7}$Ge$_{0.3}$ | 290       | 12.2                   | 50                  | 365$^b$          |              |                        | [70]       |

$^a$ Approximation from the figures in the cited papers.

$^b$ Calculated from the figures in the cited papers.
Thermal hysteresis for $\text{Mn}_{1.1} \text{Fe}_{0.9} \text{P}_{x} \text{Ge}_{y}$ ($x = 0.19, 0.22, 0.25$) were reported at 6, 4, and 2 K, respectively [65], while for $\text{Mn}_{1.2} \text{Fe}_{0.8} \text{P}_{0.76} \text{Ge}_{0.24}$ it was observed to be 8 K [69]. In order to clarify the nature of magnetic and structural transition and measure the associated $|\Delta S|$, $\text{Mn}_{1.1} \text{Fe}_{0.9} \text{P}_{0.76} \text{Ge}_{0.24}$ was studied using differential scanning calorimetry (DSC) [67]. It is also the best performing alloy in this family, as can be seen in table 2.

Improvement in MCE properties and thermal hysteresis reduction can be achieved through homogenization of chemical composition and crystal structures through heat treatment and annealing [12, 13, 72]. It was further validated with 22% improvement in MCE properties and a reduction in thermal hysteresis from 15 K to 9 K for $\text{Mn}_{1.1} \text{Fe}_{0.9} \text{P}_{0.8} \text{Ge}_{0.2}$ [66]. Another example is of $\text{Mn}_{1.1} \text{Fe}_{0.9} \text{P}_{0.76} \text{Ge}_{0.24}$, where $|\Delta S|$ was improved by 73% through a more homogenous element distribution achieved by very high cooling rate during melt-spinning [56, 73]. While $|\Delta S|$ is nearly doubled for $\text{MnFe}_{0.9} \text{P}_{0.75} \text{Ge}_{0.25}$ by increasing quenching time, although hysteresis increased from 2 K to 5 K as can be seen in table 2 [64].

2. Conclusions

For a working magnetic refrigerant, authors are of the opinion that instead of searching for new materials, already well-established families exhibiting high MCE properties should be further investigated. For this purpose, this literature review was undertaken and all compositions of MnAs, MnFeP$_{1-x}$As$_x$ and their alloys with their $T_1$ in the range 260–340 K were tabulated. In the case of MnAs and its alloys, Mn$_{0.9875}$Cr$_{0.0125}$As and Mn$_{0.9875}$G$_{0.0083}$Fe$_{0.009}$As are the best performing compositions with highest RCP, $\Delta T_{ad}$ and $|\Delta S|$ values reported in literature. It is also proposed that Mn$_{0.99}$Co$_{0.01}$As should be further scrutinized as it has displayed the highest $\Delta T_{ad}$ in this family. One of the major drawbacks of this family is the toxicity of As, which can be overcome by replacing As with Si and/or Ge, which exhibited promising results as well as hysteresis reduction. Mn$_{1.1}$Fe$_{0.9}$P$_{0.76}$Ge$_{0.24}$ and Mn$_{1.1}$Fe$_{0.9}$P$_{0.74}$Ge$_{0.26}$ are the best performing compositions in MnFeP(As/Si/Ge) family as evident from the table 2. It is therefore proposed that these compounds should be prepared with high purity starting materials and synthesized as nanostructures to further improve already promising MCE properties all the while lowering hysteresis.

A contrastive analysis of different doping/substitution materials was done for hysteresis mitigation. A large hysteresis (∼5–30 K), depending upon composition and magnetic field, is a major drawback for this family. For MnAs, different doping/substitution materials such as S, Se, Te, Bi, and P were used with unsatisfactory results because of their low solubility with MnAs. Doping of Sb, Si and interstitial N have a positive effect on the hysteresis reduction; however, MCE properties were compromised. Substitution of a small amount of Sb reduced the thermal hysteresis to about 1 K, while Si reduced it to nearly zero. For MnAs, the most successful substitution materials was done for hysteresis mitigation. A large hysteresis (∼5–30 K), depending upon composition and magnetic field, is a major drawback for this family. For MnAs, different doping/substitution materials such as S, Se, Te, Bi, and P were used with unsatisfactory results because of their low solubility with MnAs. Doping of Sb, Si and interstitial N have a positive effect on the hysteresis reduction; however, MCE properties were compromised. Substitution of a small amount of Sb reduced the thermal hysteresis to about 1 K, while Si reduced it to nearly zero. For MnAs, the most successful

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ORCID iDs

Shahid Ali https://orcid.org/0000-0002-4152-3743

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