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2015

Chen, X., & Ramanujan, R. V. (2015). The magnetic phase transition in Mn_{1.1}Fe_{0.9}P_{1-x}Gex magnetocaloric alloys. *Journal of applied physics*, 117(6), 063909-.

<https://hdl.handle.net/10356/106991>

<https://doi.org/10.1063/1.4906568>

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Citation: *Journal of Applied Physics* **117**, 063909 (2015); doi: 10.1063/1.4906568

View online: <http://dx.doi.org/10.1063/1.4906568>

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The magnetic phase transition in $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$ magnetocaloric alloys

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(Received 1 December 2014; accepted 14 January 2015; published online 13 February 2015)

Mn-Fe-P-Ge alloys are promising, low cost, high performance candidates for magnetic cooling applications based on the magnetocaloric effect. These alloys undergo a magnetic phase transition which induces a large entropy change (ΔS). Experimental and modeling studies were conducted to study this transition for varying Ge content. Landau theory and the Bean-Rodbell model were applied to $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$ ($x = 0.26, 0.3, \text{ and } 0.32$) melt spun ribbons to model the phase transition and the associated entropy change. The critical behavior of these alloys was studied. The critical composition range at which the cross over from first order to second order magnetic transition occurs was determined. The calculated thermodynamic values and critical temperatures were in good agreement with our experimental results. A high maximum entropy change (ΔS) of $\sim 44.9 \text{ J kg}^{-1} \text{ K}^{-1}$ was observed in $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.74}\text{Ge}_{0.26}$ in a 5 T applied magnetic field. The results suggest that Mn-Fe-P-Ge alloys are very attractive materials for near room temperature magnetic cooling. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4906568>]

I. INTRODUCTION

Energy efficient magnetocaloric materials and magnetic cooling systems have attracted intense research interest due to the rapid and unsustainable rise in energy consumption technologies.^{1–4} Following the discovery of the giant magnetocaloric effect (GMCE) in $\text{MnFeP}_{0.45}\text{As}_{0.55}$ alloys,⁵ low cost Mn-Fe-P-Ge based alloys were developed for applications in magnetic cooling.^{6–8} These alloys are attractive, since Ge replaced the toxic As, at the same time, the magnetocaloric effect (MCE) performance was enhanced. Besides Ge, Si has been recently studied as an alternative to As, and Mn-Fe-P-Si alloys also exhibit promising MCE.⁹ Mn-Fe-P-Ge alloys exhibit a discontinuous magnetic phase transformation from the ferromagnetic (FM) state to the paramagnetic (PM) state at the phase transition temperature (T_c), resulting in large magnetic entropy change, which leads to attractive magnetocaloric properties.^{10–15} The transition temperature (T_c) is sensitive to Ge and Mn content, which indicates that the relevant exchange energy is a strong function of interatomic spacing.¹⁶

The first order structural transition in Mn-Fe-P-Ge alloys is the lattice parameter change of hexagonal $\text{P}\bar{6}2\text{m}$ structure (Fe_2P type). Fe_2P based alloys exhibit both itinerant-electrons as well as localized spin magnetic behavior due to the two types of Fe sites (3g and 3f sites). Mn atoms can occupy both the 3g-site and 3f-site, while Fe atoms occupy only the 3f-site. Both P and Ge can occupy 1b and 2c randomly. The lattice parameter change (distance of 3f and 3g sites) can be induced by magnetic transition (paramagnetic \rightarrow ferromagnetic) of Fe atoms.^{17,18} The origin of change from first order to second order phase transition can be related to the ratio of the interatomic distance between Mn atoms to the radius of the 3d electron shell of the Mn atoms.¹⁹ The Fe atom at the 3f-site was

found to show itinerant electron behavior, while the Fe atom at the 3g-site exhibits localized spin characteristics.²⁰ With Mn substitution for Fe in Mn-Fe-P-Ge alloys, the saturation magnetization moment is much closer to the localized moment of Fe; in other words, localized spin behavior dominates in Mn-Fe-P-Ge alloys.²¹ Therefore, a model for localized magnetism is suitable for these alloys.

The mean-field scaling method²² and Bean-Rodbell model^{23–26} can be used to simulate the first- and second order transition. Since we mainly focus on the volume change during the magnetic transition, the Bean Rodbell model was applied.

The novelty of our work is to extend the Bean-Rodbell model to Mn-Fe-P-Ge alloys to determine the order of magnetic transition, and to determine the critical composition at which cross over from first order to second order phase transition occurs. It is very useful to be able to predict the order of transition, since the entropy change (ΔS) is typically several times higher in a first order transition compared to a second order transition.

In this work, we studied the magnetic phase transition experimentally and by modeling. We applied the Bean-Rodbell model to $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$ ($x = 0.26, 0.3, \text{ and } 0.32$) melt spun ribbon alloys; the critical composition was found to be $x = 0.3$, beyond which the magnetic transition crosses over from first order to second order. A large maximum ΔS of $\sim 44.9 \text{ J kg}^{-1} \text{ K}^{-1}$ in $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.74}\text{Ge}_{0.26}$ alloys was obtained in 5 T applied field, a good match of the predicted magnetic entropy change to the experimental results was obtained. In the modeling of magnetic phase transition and magnetocaloric effect in Mn-Fe-P-Ge alloys, good fit for the transition temperature as well as a good fit of the M v/s T curves are necessary.²⁷ In our case, the Bean-Rodbell model and Landau equation provided a good fit for both the transition temperature and M v/s T curves, hence a reliable calculation of refrigeration coefficient (RCE) in the second order phase transition could be achieved.

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II. EXPERIMENTAL

Polycrystalline $\text{Mn}_{1-x}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$ ($x = 0.26, 0.3, \text{ and } 0.32$) alloys were prepared by melt spinning process. They were prepared by arc melting, followed by melt spinning at 60 rpm wheel speed in argon atmosphere. These samples are designated as Ge0.26, Ge0.3, and Ge0.32. They were annealed in vacuum at 950°C for 3 h to produce the parent Fe_2P hexagonal structure.²⁰ The magnetic measurements were carried out by a commercial superconducting cryostat PPMS (Physical Property Measuring System, Quantum Design, USA), equipped with a vibrating sample magnetometer.

III. THE MODEL

Bean and Rodbell described the magnetic transition in MnAs, which can be first order when the exchange interaction is a sufficiently strong function of lattice parameter.²³

The Curie temperature (T_c) in the presence of lattice strain can be described as follows:²³

$$T_c = T_0(1 + \beta\omega), \quad (1)$$

where T_0 represents the Curie temperature in the absence of lattice compression and β is the slope of the dependence of T_c on the volume V . β can be expressed as $\beta = d(T_c/T_0)/d(V/V_0)$. ω equals to $(V-V_0)/V_0$ and is the normalized volume change (unit cell deformation). We now state the relevant expressions for the Gibbs free energy (G), normalized volume change (ω), phase transition parameter (η), entropy (S), and ion total angular momentum (J).

A. Expression for Gibbs free energy (G)

The Gibbs free energy per unit volume can be described by exchange interactions, the Zeeman effect, distortion, and pressure effects²⁵

$$G = -\frac{3}{2} \left(\frac{J}{J+1} \right) N\kappa_B T_c \sigma^2 - HM_S \sigma + \frac{1}{2K} \omega^2 + P\omega - TS, \quad (2)$$

where J is the ion total angular momentum; N is the number of magnetic atoms per unit volume; κ_B is Boltzmann's constant; M is the magnetization. M_S is the saturation magnetization value. $\sigma = M/g\mu_B JN$ is the relative magnetization at absolute temperature T ; H is the applied magnetic field. g is the Landé factor; μ_B is the Bohr magneton, K is the compressibility; P is the pressure, and S is the magnetic entropy with $S = N\kappa_B [\ln 2 - \frac{1}{2} \ln(1 - \sigma^2) - \sigma \tanh^{-1} \sigma]$.

B. Expression for normalized volume change (ω)

An expression for ω has been previously defined²³

$$\omega = (V - V_0)/V_0 = \frac{3}{2} \frac{J}{(J+1)} N\kappa_B T_0 \beta \sigma^2 - PK. \quad (3)$$

Equation (3) can be obtained by inserting Eq. (1) into Eq. (2) and minimizing the free energy with respect to the volume (V). This equation shows that the volume change is influenced by the pressure and magnetization value.

C. Expression for phase transition parameter η

By substitution of Eq. (3) into Eq. (2), minimizing the free energy with respect to σ , and setting H equal to zero, the relation between normalized spontaneous magnetization and T/T_0 is obtained as²³

$$\frac{T}{T_0} = \frac{\sigma}{\tanh^{-1} \sigma} \left(3 \frac{J}{J+1} - 3 \frac{J}{J+1} PK\beta + \frac{9}{80} \eta \frac{[(2J+1)^4 - 1]}{(J+1)^4} \sigma^2 \right), \quad (4)$$

where η is the phase transition parameter, given by

$$\eta = \frac{5[4J(J+1)]^2 N\kappa_B K T_0 \beta^2}{2[(2J+1)^4 - 1]}. \quad (5)$$

Equation (5) is the desired expression for η , η decides the order of the transition. By plotting T/T_0 v/s η , the difference between the critical and equilibrium temperatures can be obtained, which is a measure of the thermal hysteresis. For $\eta > 1$, the transition corresponds to a discontinuous change in magnetization and is first order. For $\eta < 1$, the magnetic phase transition from the ferromagnetic to the paramagnetic phase is of second order.²³

D. Expression for entropy (S)

To examine the influence of the first order and second order magnetic phase transition on the magnetocaloric properties, Eq. (6) was obtained by inserting Eqs. (3) and (4), $\sigma = M/g\mu_B JN$ and $S = N\kappa_B [\ln 2 - \frac{1}{2} \ln(1 - \sigma^2) - \sigma \tanh^{-1} \sigma]$ into Eq. (2)²⁸⁻³⁰

$$\frac{2G}{N\kappa_B T_0} = -2 \ln 2 \frac{T}{T_0} - \frac{P^2 K}{N\kappa_B T_0} - \frac{2HM_S}{N^2 \mu_B J \kappa_B g T_0} M + a_1 M^2 + a_3 M^4 + a_5 M^6, \quad (6)$$

where

$$a_1 = 3 \frac{J}{J+1} \frac{\left[\frac{T}{T_0} + (PK\beta - 1) \right]}{(g\mu_B J)^2}, \quad (7)$$

$$a_3 = \frac{9}{10} \frac{[(2J+1)^4 - 1]}{[2(J+1)]^4} \frac{\left(\frac{T}{T_0} - \eta \right)}{(g\mu_B J)^4}, \quad (8)$$

$$a_5 = \left[\frac{27}{25} \left(\frac{J}{J+1} \right)^3 \frac{[(2J+1)^4 - 1]^2}{[4J(J+1)]^4} - \frac{18}{35} \left(\frac{J}{J+1} \right)^6 \frac{[(2J+1)^6 - 1]}{(2J)^6} \right] \frac{T}{(g\mu_B J)^6}. \quad (9)$$

From Landau theory and the expansion of free energy with respect to magnetization, a first-order magnetic transition occurs when $a_1 > 0$, $a_3 < 0$ while $a_5 > 0$.³¹

By inserting Eq. (3) in Eq. (2) and minimizing Gibbs free energy with respect to σ , the magnetic state equation can be expressed by the Brillouin function³²

$$\sigma = B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}Y\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}Y\right), \quad (10)$$

where²⁴

$$Y = \frac{1}{T} \left[3T_0 \sigma \left(\frac{J}{J+1} \right) (1 - PK\beta) + \frac{9}{5} \left\{ \frac{(2J+1)^4 - 1}{[2(J+1)]^4} \right\} T_0 \eta \sigma^3 + \frac{g\mu_B J}{\kappa_B} H \right]. \quad (11)$$

The entropy can be obtained from the inverse Brillouin function $B_J^{-1}(\sigma) = -\frac{1}{N\kappa_B} \frac{\partial S}{\partial \sigma}$,²⁴ from which one can obtain the temperature, pressure, and magnetic field dependence of entropy.^{23,33} Equation (12) is the desired expression for S.

$$S(T, P, H) = R \left[\ln(Z) + T \frac{\partial \ln(Z)}{\partial T} \right], \quad (12)$$

where

$$Z = \frac{\sinh \left[\left(\frac{2J+1}{2J} \right) Y \right]}{\sinh \left(\frac{Y}{2J} \right)}. \quad (13)$$

E. Expression for ion total angular momentum (J)

In the $\text{Mn}_{1-x}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$ alloys, localized magnetism arises from Mn and Fe ions. To determine the value of the ion total angular momentum (J), the Brillouin function and Curie law were applied.³⁴

For $\chi \ll 1$, M can be expressed by

$$M = N_A g \mu_B J B_J(x) = \frac{N_A g^2 \mu_B^2}{3\kappa_B T} J(J+1) H, \quad (14)$$

where χ is the molar susceptibility, J is the ion total angular momentum, and N_A is Avogadro's constant.

The molar susceptibility (χ) is given by

$$\chi = \frac{M}{B} = \frac{N_A \mu_B^2}{3\kappa_B T} g^2 J(J+1) B = \frac{C_M}{T}, \quad (15)$$

where C_M is the Curie constant which is defined by

$$C_M = \frac{N_A \mu_B^2}{3\kappa_B} g^2 J(J+1) = \frac{N_A \mu_B^2}{3\kappa_B} P_{eff}^2 \approx \frac{1}{8} P_{eff}^2 \quad (16)$$

and P_{eff} is the dimensionless effective magnetic moment $P_{eff} = g\sqrt{J(J+1)}$.

IV. RESULTS AND DISCUSSION

Fig. 1 shows the magnetic properties (Fig. 1(a)) and the entropy change as a function of temperature (Fig. 1(b)) of the Ge0.26 alloy. The M v/s T plots for Ge0.26, Ge0.3, and Ge0.32 alloys (Fig. 1(c)) and the entropy change for these alloys for 5 T field are shown (Fig. 1(d)).

The phase transition parameter (η) was determined by matching the experimental T v/s σ curve with the curves calculated from Eq. (4) for a range of η values (Fig. 2). The resulting values of η , T_0 , and T_c are listed in Table I for Ge0.26, Ge0.3, and Ge0.32 alloys. The good fit of the experimental results with the Bean-Rodbell model can be demonstrated by examining the match between the modeling results and the experimentally obtained curves of ΔS v/s T in 5 T field for Ge 0.26, Ge0.3, and Ge0.32 (Fig. 3).

A. Phase transition parameter η

For the Ge0.26 sample, a J value of 0.51 was calculated from Eqs. (19) and (20). Since the ion total angular momentum is quantized and can be $1/2, 1, 3/2, 2, 5/2, \dots$, a value of $1/2$ was used as the value of J . The saturation magnetization of Ge0.26 ribbon in a 1 T magnetic field ($3.5 \mu\text{B}/\text{f.u.}$) was determined by magnetization measurement at 10 K (Fig. 1(a)).

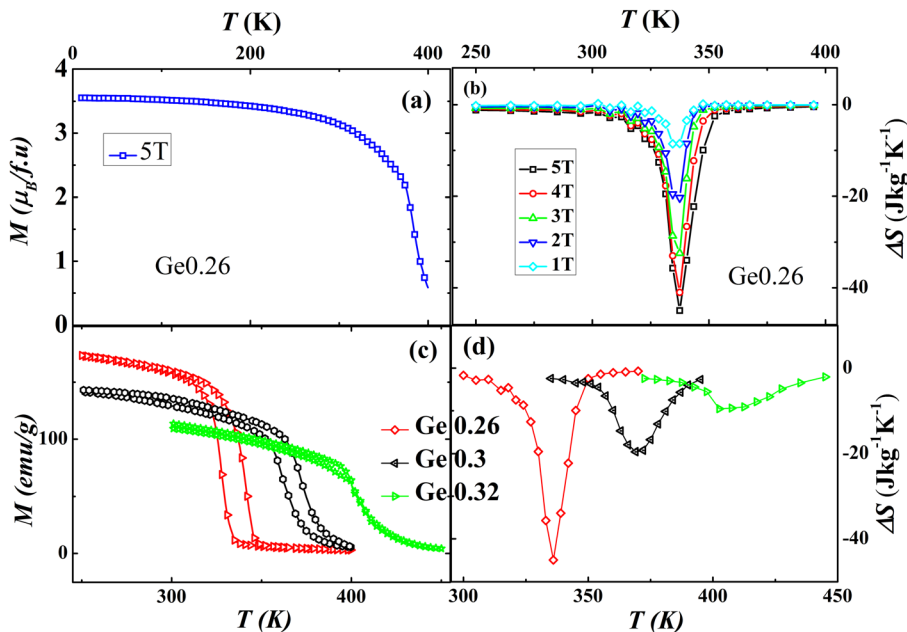


FIG. 1. (a) FCC $M(T)$ curves in 5 T magnetic field of Ge0.26 alloy. (b) Temperature dependence of magnetic entropy change (ΔS_M) in 1 T, 2 T, 3 T, 4 T, and 5 T of Ge0.26 alloy. (c) FCC and FCW $M(T)$ curves in 1 T applied magnetic field of Ge0.26, Ge0.3, and Ge0.32 alloys. (d) ΔS_M of Ge0.26, Ge0.3, Ge0.32 alloys in 5 T applied magnetic field.

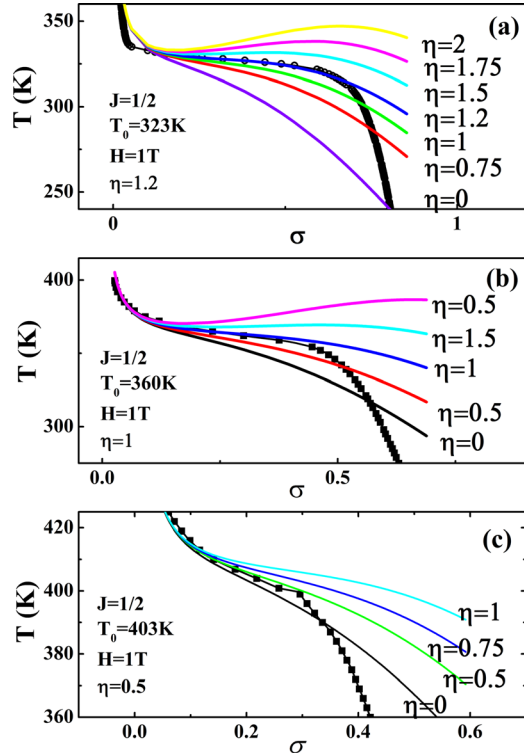


FIG. 2. Experimental temperature dependence of relative magnetization in 1 T external magnetic field of Ge0.26, Ge0.3, and Ge0.32 alloys (curves with symbol) compared to the modeling results of Bean-Rodbell Model for a range of η (plain curves).

The Curie constant C_M can be experimentally determined from the experimental M v/s T curves ($1/\chi = H/M$) (Fig. 1), since $\frac{1}{C_M}$ is the slope of $\frac{1}{\chi}$ v/s T curve. By inserting $g = 2$ (theoretical value) and the experimental value of C_M in Eqs. (19) and (20), the J value of $Mn_{1.1}Fe_{0.9}P_{1-x}Ge_x$ alloys were obtained (Table I).

By minimizing Eq. (6) with respect to M and setting the value of the resulting equation to zero, Eq. (17) was obtained

$$-\frac{2HM_S}{N^2\kappa_B\mu_B gJT_0} + 2a_1M + 4a_3M^3 + 6a_5M^5 = 0. \quad (17)$$

Inserting Eqs. (7)–(9) and the relationship $\sigma = M/g\mu_B JN$ into Eq. (17), Eq. (18) can be obtained

$$T = \left(\frac{2HM_S}{N\kappa_B} + 2T_0\sigma + 0.67T_0\eta\sigma^3 \right) / (0.65\sigma^5 + 0.67\sigma^3 + 2\sigma). \quad (18)$$

By inserting the theoretical value of g (equal to 2), the parameters from experimental data ($J = 1/2$, $N = 2$,

TABLE I. List of ion total angular momentum (J), phase transition parameter (η), T_0 and T_c values of Ge0.26, Ge0.3, and Ge0.32 alloys.

X	0.26	0.3	0.32
J_{cal}	0.51	0.37	0.35
η	1.2	1	0.5
T_0 (K)	323	360	403
T_c (K)	326.9	370.4	397

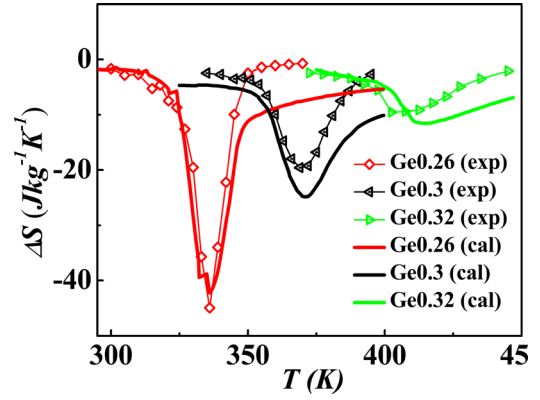


FIG. 3. Theoretical and experimental results of temperature dependence of isothermal magnetic entropy change for magnetic field change from 0 to 5 T in Ge0.26, Ge0.3, and Ge0.32 alloys.

$M_S = 3.5 \mu_B/\text{f.u.}$, $H = 1 \text{ T}$), $\kappa_B = 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$ and $\mu_B = 9.27 \times 10^{-24} \text{ J T}^{-1}$, a relationship between σ and T can be obtained

$$T = (2.4 + 2T_0\sigma + 0.67T_0\eta\sigma^3) / (0.65\sigma^5 + 0.67\sigma^3 + 2\sigma). \quad (19)$$

Fig. 2 shows the matching of the experimental and calculated (from Eq. (19)) relation between temperature (T) and relative magnetization (σ) of the Ge0.26, Ge0.3, and Ge0.32 alloys in a 1 T external magnetic field. With increasing Ge content, the phase transition parameter η decreases, and it is less than 1 for Ge0.32. This is consistent with the experimental M v/s T curves for this alloy, which indeed exhibits a second order transition. The experimental M v/s T results for the Ge0.3 alloy in Fig. 1 show a thermal hysteresis of $\sim 10 \text{ K}$, which is a sign of a first order transition. Rice³⁵ pointed out that for η equal to 1, the transition is first order, with an associated latent heat and discontinuous volume change at the transition point. Thus, the cross over from first order to second order transition occurs in the composition range of $0.3 < x < 0.32$.

B. Isothermal magnetic entropy change

Since we are interested in the isothermal magnetic entropy change of these Mn-Fe-P-Ge alloys, we use the value $J = 1/2$, $g = 2$ for the Ge0.26, Ge0.3, and Ge0.32 alloys at zero pressure. By inserting these values into Eqs. (11)–(13), the magnetic entropy change can be expressed as

$$\Delta S_{\text{mag}}(T, H) = S_{\text{mag}}(T, H_f) - S_{\text{mag}}(T, H_0) = R \left\{ \ln \frac{Z_{H_f}}{Z_{H_0}} + T \left[\frac{\partial \ln(Z_{H_f})}{\partial T} - \frac{\partial \ln(Z_{H_0})}{\partial T} \right] \right\}, \quad (20)$$

where

$$Z = \frac{\sinh(2Y)}{\sinh(Y)} = e^Y + e^{-Y} \quad (21)$$

and

$$Y = \frac{1}{T} (T_0 \sigma + 0.67 T_0 \eta \sigma^3 + 0.67 H). \quad (22)$$

H_0 and H_f are the initial and maximum applied field.

Fig. 3 shows the fitting of the calculated magnetic entropy change of Ge0.26, Ge0.3, and Ge0.32 alloy in 5 T external magnetic field from Eqs. (20)–(22) using the experimental M vs. T data and the experimental results of ΔS (Fig. 1). The parameters T_0 and η , determined by fitting with the experimental data in Fig. 2, were again used in these calculations. The calculated ΔS exhibits good agreement with the experimental results for the Ge0.26 alloy. For other alloy compositions, there is reasonable agreement between the model and experiment for the Ge0.3 and Ge0.32 alloys for temperatures less than T_c .

V. CONCLUSIONS

The magnetocaloric effect in Mn-Fe-P-Ge alloys was investigated experimentally and by the Bean-Rodbell model. Good agreement was found between the experimental data and the modeling results. In Mn-Fe-P-Ge alloys, the magnetic transition can be first-order and second-order. With increasing Ge content, it was predicted that the magnetic transition changes from first to second order in the critical range of $0.3 < x < 0.32$. $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.74}\text{Ge}_{0.26}$ exhibits highest ΔS of $\sim 44.9 \text{ J kg}^{-1} \text{ K}^{-1}$ in 5 T applied field near room temperature.

ACKNOWLEDGMENTS

This research is conducted by NTU-HUJ-BGU Nanomaterials for Energy and Water Management Programme under the Campus for Research Excellence and Technological Enterprise (CREATE), that was supported by the National Research Foundation, Prime Minister's Office, Singapore.

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