

The sign of lattice and spin entropy change in the giant magnetocaloric materials with negative lattice expansions

Jia-Zheng Hao^{a,b}, Feng-Xia Hu^{b,c,d,*}, Zi-Bing Yu^{b,c}, Fei-Ran Shen^{b,c}, Hou-Bo Zhou^{b,c}, Yi-Hong Gao^{b,c}, Kai-Ming Qiao^{b,c}, Wen-Hui Liang^{b,c}, Jia Li^{b,c}, Cheng Zhang^{b,c}, Jing Wang^{b,c,e}, Jun He^{a,*}, Ji-Rong Sun^{b,c,d}, Bao-Gen Shen^{b,c,d}

^a Division of Functional Material Research, Central Iron and Steel Research Institute, Beijing 100081, PR China

^b Beijing National Laboratory for Condensed Matter Physics & State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, PR China

^c School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, PR China

^d Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, PR China

^e Fujian Innovation Academy, Chinese Academy of Sciences, Fuzhou, Fujian 350108, PR China

ARTICLE INFO

Keywords:

Sign of lattice entropy change
Sign of spin entropy change
Negative lattice expansion
Magnetocaloric effect

ABSTRACT

Solid-state refrigeration based on the magnetocaloric effect (MCE) has garnered worldwide attention because of its superior energy conservation and its environmentally friendly impact. Many materials exhibiting magnetostructural/magnetoelastic transitions have been identified by their giant MCE as promising refrigerants. The common feature of these materials is their simultaneous magnetic and lattice transitions; some also undergo negative expansions, i.e., lattice contractions, along with a ferromagnetic (FM) to paramagnetic (PM) transition. For these materials, whether the signs of lattice and spin entropy change are the same or opposite has become a controversial issue, noting that a larger unit cell volume usually indicates softer phonons and therefore a bigger phonon entropy. On the basis of our experiments and published data, we demonstrate that the lattice and spin entropy changes retain the same sign at least for La(Fe,Si)₁₃-based compounds and MM'X alloys with giant MCE, for which the lattice undergoes negative expansion along with a FM to PM transition on heating. The clarification of the sign of lattice entropy change in the total entropy change is of particular importance for a comprehensive understanding of new materials with giant magnetocaloric effect and their design.

1. Introduction

Solid-state cooling based on the magnetocaloric effect (MCE) is a promising alternative to traditional vapor compression refrigeration because of its environment-friendly impact and in theory high energy efficiency [1–4]. Since the discovery of the giant MCE in Gd₅(Si₂Ge₂), a number of first-order giant magnetocaloric materials have been discovered [5–17], which in turn promoted the development of the magnetic refrigeration technique. A common feature of these materials is that magnetic phase transition is always accompanied by a discontinuous change in lattice parameter and/or crystal symmetry. The giant MCE originates from a concurrent structural and magnetic transition. Rough estimations show that the lattice contribution accounts for 50%–60% or more of the total entropy change for the materials undergoing a magnetostructural/magnetoelastic transition [5,7], and

the magnitude of lattice entropy change (ΔS_{Latt}) is closely related to the volume change ($\Delta V/V$) during the phase transition [7]. However, positive [8,9] or negative [3,10–13,15–17] lattice expansions may occur along with a ferromagnetic (FM) to paramagnetic (PM) transition among the different materials with giant MCE.

Typically, Gd₅(Si_xGe_{1-x})₄ undergoes a positive expansion from a FM orthorhombic α -Gd₅Si₂Ge₂ to a PM monoclinic β -Gd₅Si₂Ge₂ structure with $\Delta V/V \sim +(0.4\text{--}1.0)\%$ [8,9]. Generally, a larger lattice volume indicates softer phonons and therefore a larger phonon entropy. Hence, understandably, the sign of ΔS_{Latt} is the same as that for the spin entropy change (ΔS_{Spin}) during the magnetostructural transition in Gd₅(Si_xGe_{1-x})₄. Note that the spin entropy of the PM state is also larger than that of the FM state. In contrast, some materials with giant MCE show negative expansions, i.e., lattice contractions, during the FM to PM transition. For example, La(Fe,Si)₁₃-based compounds undergo a

* Corresponding authors at: Beijing National Laboratory for Condensed Matter Physics & State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, PR China (F.X. Hu).

E-mail addresses: fxhu@iphy.ac.cn (F.-X. Hu), hejun@cisri.com.cn (J. He).

<https://doi.org/10.1016/j.jmmm.2020.166983>

Received 20 January 2020; Received in revised form 25 March 2020; Accepted 6 May 2020

Available online 08 May 2020

0304-8853/© 2020 Elsevier B.V. All rights reserved.

magnetoelastic phase transition with a space group (Fm-3c) unchanged while the lattice contracts by $\Delta V/V \sim (1.2-1.6)\%$ on heating during the FM to PM transition [3,10,18]. MnAs-based compounds undergo a magnetostructural transition from a FM hexagonal NiAs-type to a PM orthorhombic MnP-type structure, and the lattice contracts by $\Delta V/V \sim (1.1-2.1)\%$ [12,13]. Furthermore, an abnormal lattice contraction with $\Delta V/V \sim (2.8-3.9)\%$ occurs in MnCoGe/MnNiGe-based alloys during the magnetostructural transition from a FM/AFM orthorhombic TiNiSi-type to a PM hexagonal Ni₂In-type structure [16,17,19,20]. For these materials, whether the sign of lattice and spin entropy change is the same or opposite has always been controversial and has puzzled many researchers [21–23], noting that the lattice parameter of the FM/AFM phase is larger than that of the PM phase. In general, an application of a magnetic field, which drives the system from a PM to a FM state, should increase the lattice entropy while simultaneously decreasing the spin entropy. The signs of lattice and spin entropy change should be opposite. Similar to La(Fe,Si)₁₃, the magnetic and structural transitions in MnAs also cannot be separated. A study on MnAs based on density functional theory (DFT) concluded that the phonon contribution to the total entropy change has the opposite sign to the spin entropy change [24], although no direct experimental evidence has been reported to date. For La(Fe,Si)₁₃, Jia and coworkers in our group once believed the spin entropy change was negative, whereas the phonon entropy change was positive but smaller, hence leading to an overall negative entropy change upon applying a magnetic field [21]. However, recent experimental investigations indicated that this is not the case. Landers and co-workers investigated the lattice vibrational entropy change ΔS_{Latt} in LaFe_{11.6}Si_{1.4} by nuclear resonant inelastic X-ray scattering (NRIXS) [22,23]. The results demonstrated that the ΔS_{Latt} obtained by this method is a sizable quantity and contributes cooperatively to the total entropy change ΔS during the phase transition for La(Fe,Si)₁₃ compounds. Moreover, earlier studies on the stoichiometric MnCoGe and MnNiGe alloys with separated structural and magnetic phase transitions indicated that the signs of ΔS_{Latt} and ΔS_{Spin} are the same although the alloys undergo negative expansion during the structural transition [19,20]. In this paper, we present the details.

2. Results summarized based on literatures and our experiments

2.1. MM'X alloys

As members of the MM'X family (M, M' = transition elements, X = main element), the MnCoGe-based and MnNiGe-based alloys undergo negative thermal expansions along with FM/AFM to PM transitions [16,19,20,25–30]. The reported giant MCE originates from concurrent structural and magnetic transitions. This situation also pertains to La(Fe,Si)₁₃ and MnAs materials. Fortunately, the structural and magnetic transitions can be separated by adjusting the composition of the MM'X alloys.

Previously, Johnson in 1975 and Anzai and Ozawa in 1978 [19,20] studied the magnetic and structural characteristics of the stoichiometric MnCoGe and MnNiGe alloys, which show separated structural and magnetic phase transitions. The martensitic structural transition T_M occurs in the PM region, and is accompanied by a pronounced lattice expansion with $\Delta V/V \sim (1.6-3.9)\%$ upon cooling (Fig. 1a). From the heat flow measured by differential scanning calorimetry (DSC) or differential thermal analysis (DTA) (Fig. 1b, c), the sign of phase transition heat is seen to be the same as for the discrete magnetic and structural phase transitions of MnCoGe and MnNiGe, obeying the basic principle of increasing entropy. The materials continuously absorb heat and increase entropy while undergoing the two transitions on heating, although a negative lattice expansion occurs around T_M for both alloys.

Furthermore, Anzai and Ozawa studied the effect of pressure on these magnetic and structural transitions for MnNiGe [20]. The magnetic and structural transitions were found to couple together gradually with increasing pressure (Fig. 1c). Therefore, the heat of the phase

transition includes both magnetic and structural contributions. These results further proved that, although the structural transition is from a large volume phase to a small volume phase, the phase transition remains a process involving an increase in entropy that is the same as that for a pure magnetic transition from order (the FM/AFM phase) to disorder (the PM phase).

In addition, to obtain large MCE in the MM'X alloys, much effort has been expended in creating a magnetostructural coupling in these systems. Bao and coworkers in our group studied the magnetostructural transition and the MCE in MnCoGe_{1-x}Al_x. Replacing Ge by Al atoms stabilizes the hexagonal phase and shifts T_M to a lower temperature [31]. As a result, a magnetostructural transition was realized for compositions MnCoGe_{1-x}Al_x ($x = 0.01, 0.02$). Further increases in Al content to $x = 0.03$ lead to a shift in T_M to a lower temperature with the magnetic and structural transitions becoming separated again. For composition MnCoGe_{0.97}Al_{0.03}, the main difference from the stoichiometric MnCoGe and MnNiGe is that the structural transition (still with a negative expansion) occurs at the FM martensitic phase region (instead of the PM region) and the pure FM-PM magnetic transition occurs in the austenitic phase region. We measured the heat flow using DSC for MnCoGe_{0.97}Al_{0.03} (Fig. 2), and found that the sign of phase transition heat is also the same for the discrete magnetic and structural transitions. We calculated the entropy change with temperature using $S_{\text{Tot}}(T) - S_{\text{Tot}}(T_0) = \int_{T_0}^T \frac{1}{T} Q dT$, where Q denotes the heat flow and T the heating/cooling rate (Fig. 2). On heating, the entropy continuously increases when undergoing these two transitions. Note that the low-temperature peak of heat flow is much higher than the high-temperature peak (Fig. 2), implying that the contribution of structural transition around T_M is far greater than the pure magnetic transition (FM to PM) around T_C . By adjusting compositions, for example, MnCoGe_{1-x}Al_x ($x = 0.01, 0.02$), the magnetic and structural transitions may couple together [see our previous work, Ref. 31], and the heat of the phase transition becomes a superposition of magnetic and structural contributions.

2.2. La(Fe,Si)₁₃-based compounds

As outstanding refrigeration materials, La(Fe,Si)₁₃-based compounds with giant MCE have attracted extensive attention since their discovery in 2000 [3,32]. For these compounds, the first-order magnetic transformation from the FM to the PM state is accompanied by an abrupt isostructural negative lattice expansion with $\Delta V/V \sim (1.2-1.6)\%$ [3,10,18]. The correlation between the itinerant electron metamagnetic transition and the large magnetovolume effect was demonstrated from first-principles calculations [11,33]. The giant MCE originates from the magnetic field-induced itinerant electron metamagnetic transition from the PM to the FM state and the concurrent lattice expansion. In other words, the total entropy change is the sum of contributions from the magnetic, lattice, and electronic degrees of freedom. To understand the giant MCE thoroughly, distinguishing spin, lattice, and electron contributions is necessary. Unfortunately, unlike the MnCoGe-based alloys, the lattice entropy change of LaFe_{13-x}Si_x is difficult to obtain because the lattice and magnetic transitions cannot be separated. Therefore, whether the signs of lattice and spin entropy change are the same or opposite remains debate [21–23].

Jia and coworkers in our group investigated the entropy changes associated with the first-order magnetic transition in LaFe_{13-x}Si_x involving the respective contributions from spin and lattice [21]. The reported spin entropy change calculated by mean-field-theory was negative whereas the phonon entropy change estimated from the Debye approximation was positive but smaller. Hence, upon applying a magnetic field, the overall negative entropy change appeared. However, subsequent investigations performed by Landers and co-workers demonstrated different results for La(Fe,Si)₁₃. In 2015 and 2018, they investigated the lattice vibrational entropy change ΔS_{Latt} in

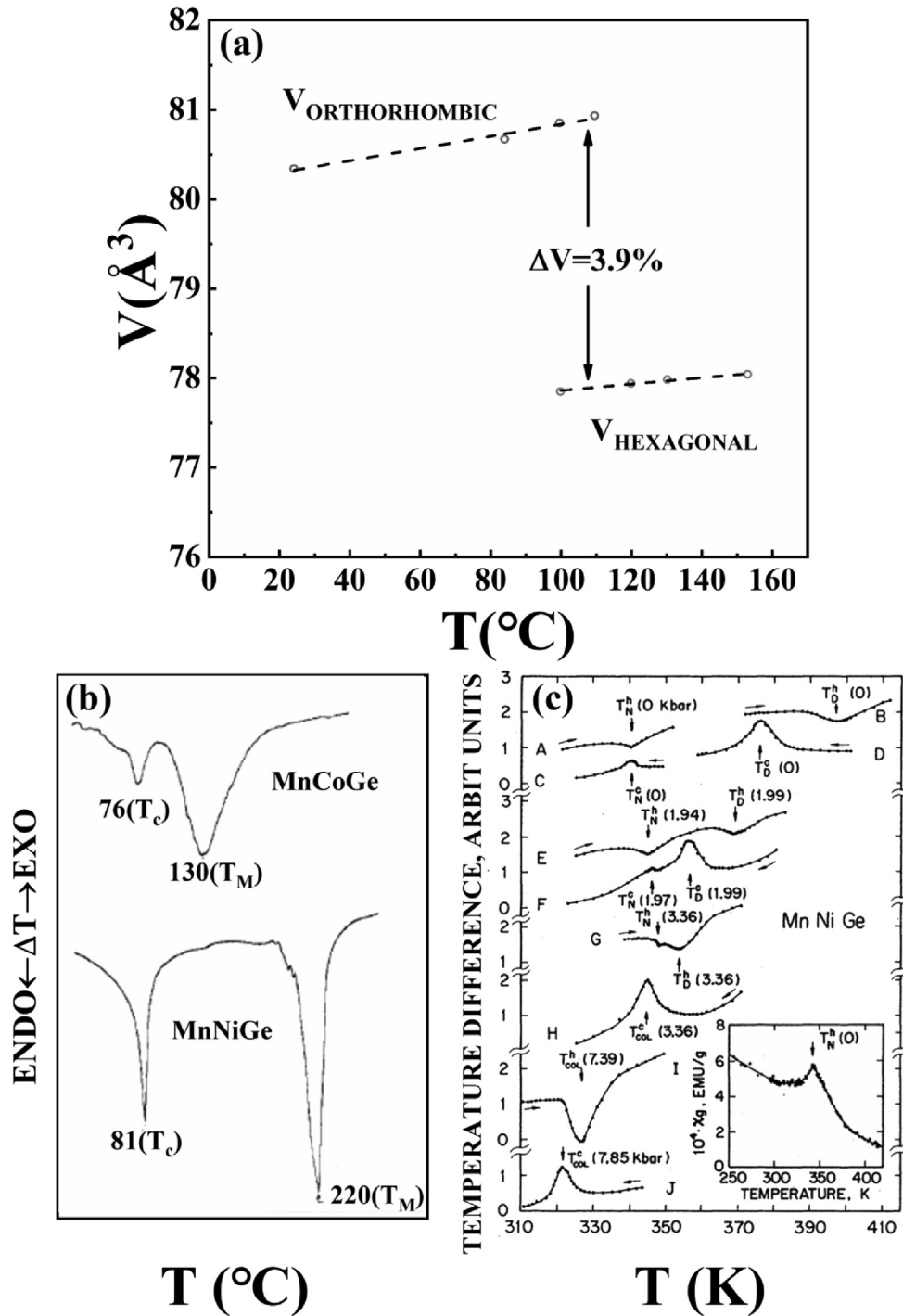


Fig. 1. (a) Temperature dependence of lattice volume for MnCoGe with structural transition at $T_M = 125$ $^\circ\text{C}$, (b) DSC traces of endothermic peaks for MnCoGe and MnNiGe, for which T_c is the Curie temperature and T_M is the structural transition temperature on heating (Reprinted with permission from [19]. Copyright 1975, ACS Publishing Limited). (c) DTA patterns for MnNiGe under various pressures; the numerical values in parentheses are the pressures in kbars. (Reprinted with permission from [20]. Copyright 1978, APS Publishing Limited).

LaFe_{11.6}Si_{1.4} using NRIXS [22,23]. The results indicated that the ΔS_{Latt} is a sizable quantity and contributes directly and cooperatively to the total entropy change ΔS at the phase transition. Since NRIXS is not sensitive to the magnetic degrees of freedom, it has proven to be a unique experimental method to determine the contribution of specific vibrations to entropy changes for 3d transition metals. The work of Landers and coworkers provided direct experimental evidences demonstrating the same signs of lattice and spin entropy change for La(Fe,Si)₁₃. They performed temperature-dependent ⁵⁷Fe NRIXS

measurements of the vibrational (phonon) density of states (VDOS) in LaFe_{11.6}Si_{1.4} across the magnetoelastic first-order phase transition T_C (Fig. 3). There is a phonon peak near 27 meV in the ferromagnetic VDOS. With increasing temperature, the temperature-induced magnetic disturbances cause the high-energy phonon peaks to disappear in the PM state. This indicates that the phonon softens in the PM state, corresponding to a significant increase in the vibration entropy change ΔS_{Latt} associated with the Fe subsystem. They also calculated the VDOS (thick red lines in Fig. 3) of LaFe_{11.6}Si_{1.4} using a generalized gradient

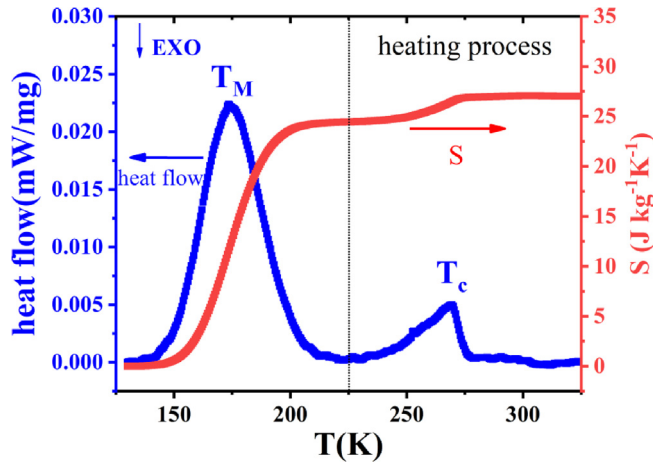


Fig. 2. Temperature dependence of heat flow (blue, endothermic curve) and entropy (red) of MnCoGe_{0.97}Al_{0.03} alloy measured on heating. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

approximation in the DFT framework. The results agree well with the experimental results (Fig. 3).

From the experimental VDOS, an abrupt increase (jump) in the Fe-partial vibrational entropy change ΔS_{Latt} was inferred, and the increased magnitude of ΔS_{Latt} is substantial in comparison with the isothermal entropy change obtained using Maxwell relation. They calculated the lattice entropy from the VDOS experimental data measured at a specific temperature using the thermodynamic relation $S_{\text{lat}}(T) = 3k_B \int_0^\infty gE \left[\frac{\beta E (e^{\beta E} + 1)}{2(e^{\beta E} - 1)} - \ln(e^{\beta E/2} - e^{-\beta E/2}) \right] dE$ [23]. The results (Fig. 4a) show that on heating the Fe-partial vibrational entropy suddenly increases with the change in state from FM to PM. The magnitude of vibrational entropy change is $6.9 \text{ J kg}^{-1} \text{ K}^{-1}$, and the lattice degree contributes cooperatively with $\sim 38\text{--}29\%$ to the total entropy obtained for LaFe_{11.6}Si_{1.4} using Maxwell relation. Furthermore, Landers and coworkers also compared the DFT-computed vibrational entropy $S_{\text{Latt}}(T)$ at constant volume for the FM, PM, and fixed spin moment (FSM) states with the experimental results (Fig. 4b) [23]. Both the experimental and theoretical results indicate that an increase in S_{Latt} occurs with the FM to PM transition on heating. Furthermore, they also presented the values of the Debye temperature Θ_D (Fig. 4c), calculated from the Lamb–Mössbauer factor f_{LM} [34]. Clearly, Θ_D drops by $\sim 4\%$ from $\Theta_D \sim 363 \text{ K}$ in the FM phase to $\Theta_D \sim 348 \text{ K}$ in the PM phase. According to the Debye approximation [5,35] $S_{\text{Latt}} = -3Nk_B \ln \left[1 - \exp\left(-\frac{\Theta}{T}\right) \right] + 12Nk_B \left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx$, a decrease in Θ_D implies an increase in the lattice entropy S_{Latt} . These results further verify that the transition from a large FM phase to a small PM phase is a process involving an increase in lattice entropy. This is consistent with our results reported recently [36]. Fig. 4d shows $\Theta_D(T)$ calculated according to the specific heat measurement at low temperature and from $\Theta_D = \Theta_0(1 - \gamma\omega)$ for La(Fe_{0.92}Co_{0.08})_{11.9}Si_{1.1} [36]. The trend in Θ_D with temperature is consistent with Fig. 4c although the absolute value of Θ_D is slightly different possibly because of subtle differences in the components between LaFe_{11.6}Si_{1.4} and La(Fe_{0.92}Co_{0.08})_{11.9}Si_{1.1}. For La(Fe_{0.92}Co_{0.08})_{11.9}Si_{1.1}, Θ_D drops by $\sim 3\%$ (Fig. 4d) from $\Theta_D \sim 300 \text{ K}$ (FM) to $\Theta_D \sim 292 \text{ K}$ (PM), which is comparable to but somewhat smaller than that for LaFe_{11.6}Si_{1.4} (Fig. 4c). This is reasonable considering that the latter, with a first-order transition, experiences a larger $\Delta V/V$ than the former [3]. All these results prove that the lattice contribution is still a process involving increasing entropy on heating despite the PM phase having a smaller volume than the FM phase.

In addition, the studies by Landers and co-workers [22,23] showed that, for the La(Fe,Si)₁₃-based compounds, a different mechanism based

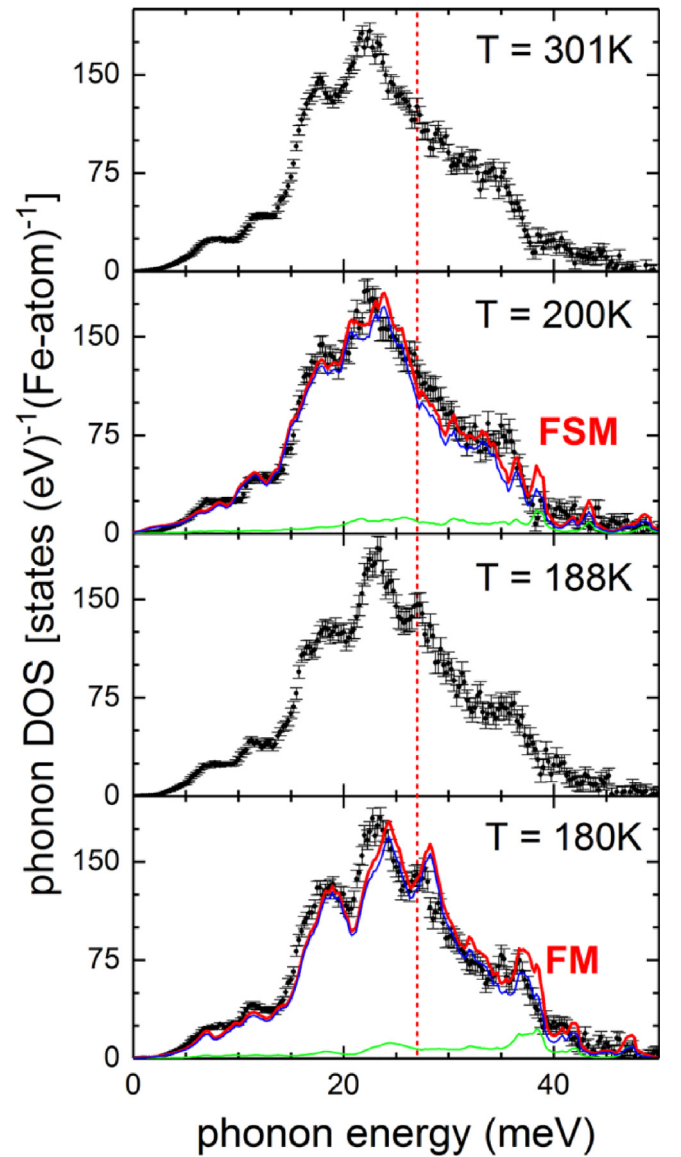


Fig. 3. Typical Fe-partial vibrational density of states (VDOS) of LaFe_{11.6}Si_{1.4} obtained from ⁵⁷Fe NRIXS measured at 301 K, 200 K, 188 K, and 180 K in a magnetic field $\mu_0 H \sim 0.7 \text{ T}$ (black circles with error bars). Red curves are DFT-computed Fe-partial VDOS for the ferromagnetic (FM) state and the fixed spin moment (FSM) state. Thick lines show the calculated Fe-partial VDOS of (96i) Fe_{II} (blue) and (8b) Fe_I sites (green). (Reprinted with permission from [23]. Copyright 2018, APS Publishing Limited). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

on adiabatic electron–phonon coupling dominates the magnetoelastic interactions, which derives solely from local changes in the electronic structure. Fig. 5 shows the partial electronic density of states DOS(E) for the minority *d* channel of Fe_I and Fe_{II} of LaFe_{11.5}Si_{1.5}, which were computed using DFT for FM, PM, and the FSM states. For both Fe sites, DOS(E) for the FM state shows close to half of the minority channels, and more importantly, a deep mid-d-band minimum was found at the Fermi level. However, the Fe-resolved minority band DOS(E) for the PM state does not show d-band minimum near Fermi level. With this change in the minority DOS(E) at the Fermi energy with temperature, adiabatic electron–phonon coupling (magnetoelastic coupling) occurs. This coupling results in phonon softening in the PM state. Moreover, the magnetic moment was calculated using DFT, and the average spin moment obtained was $2.2 \mu_B/\text{Fe}$ and $1.7 \mu_B/\text{Fe}$ for the FM and PM

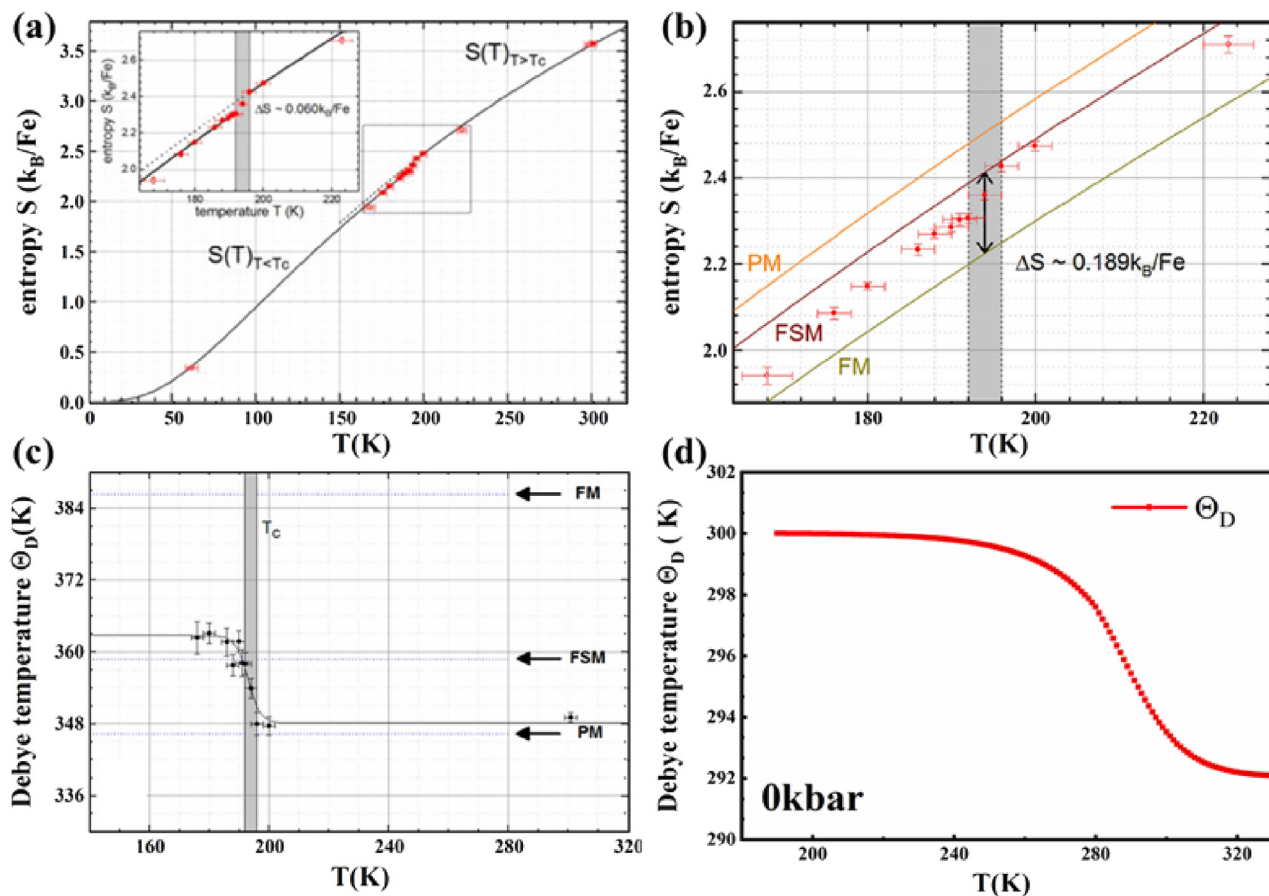


Fig. 4. Temperature dependence of the experimental (a) and DFT-computed (b) vibrational entropy $S_{\text{lat}}(T)$ of the Fe sublattice for $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound. (c) Temperature dependence of the Debye temperature Θ_D of the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound (Reprinted with permission from [23]. Copyright 2018, APS Publishing Limited). (d) Temperature dependence of Θ_D for $\text{La}(\text{Fe}_{0.92}\text{Co}_{0.08})_{11.9}\text{Si}_{1.1}$ calculated using the Debye approximation [36].

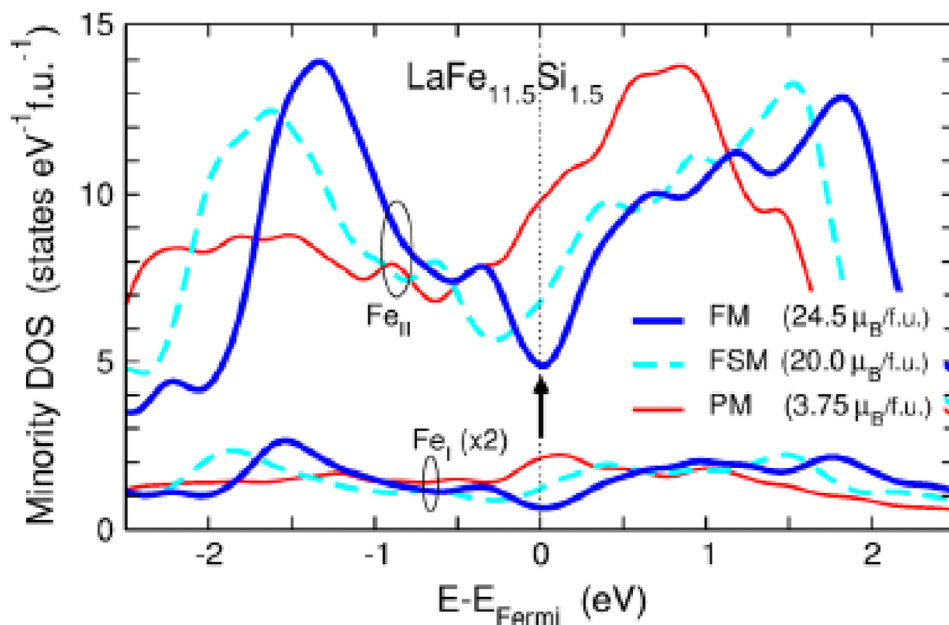


Fig. 5. DFT-computed $\text{DOS}(E)$ for minority d electrons of Fe_{II} (upper lines) and Fe_{I} (lower lines) in $\text{LaFe}_{11.5}\text{Si}_{1.5}$ (Reprinted with permission from [23]. Copyright 2018, APS Publishing Limited).

states, respectively. The decrease in Fe moment easily explains this softening phenomenon. The Fe moment changed at T_C , which shifts the stable minimum in the minority DOS away from the Fermi level, thereby reflecting the destructive changes in the VDOS around T_C and the itinerant electron metamagnetism. Furthermore, a much larger DOS at the Fermi level in the PM phase shields nuclear charges, allowing larger atomic motions (i.e., softer phonons). This also indicates that any theoretical description of the magnetoelastic transition and the lattice entropy change of La(Fe,Si)₁₃-based compounds needs to consider changes in the electronic band structure across the transition.

The above results show that, in the La(Fe,Si)₁₃-based compounds, the mechanisms based on adiabatic electron-phonon coupling dominate the magnetoelastic interactions and lead to a pronounced magneto-elastic softening despite the large volume decreases at the transition. Therefore, for La(Fe,Si)₁₃-based compounds, the sign of lattice vibration entropy change is the same as that of spin entropy change and contributes cooperatively to the total entropy change across the magnetoelastic transition.

3. Conclusion

We demonstrated that the lattice and spin entropy changes retain the same sign at least in La(Fe,Si)₁₃-based compounds and MM'X alloys with giant MCE, for which the lattice undergoes negative expansion along with a FM-to-PM transition. For MM'X alloys, heat flow measurements using DSC or DTA indicated that the sign of the phase transition heat is the same for the discrete magnetic and structural phase transitions. In addition, calculations of entropy changes based on heat flow data in MnCoGe_{0.97}Al_{0.03} alloy further prove that the entropy change from spin ordering to disordering (FM to PM) and lattice contractions were both positive, and the contribution of the lattice is far greater than that of the spin. However, the underlying mechanism is still unclear and needs further research. For La(Fe,Si)₁₃-based compounds, the combination of NRIXS and DFT based on first-principles calculations, performed by Landers and co-workers, revealed that adiabatic electron-phonon coupling leads to a pronounced magneto-elastic softening despite a large decrease in volume at the transition. This result makes evident that the sign of lattice vibration entropy change is the same as that of spin entropy change, and the both contribute cooperatively to the total entropy change across the magnetoelastic transition. Based on our experiments and published data, the sign of the contribution from lattice entropy change to the total entropy change of alloy systems with negative lattice expansions has been clarified, thereby allowing a more comprehensive understanding and regulation of giant magnetocaloric materials.

CRediT authorship contribution statement

Jia-Zheng Hao: Conceptualization, Formal analysis, Writing - original draft. **Feng-Xia Hu:** Conceptualization, Formal analysis, Writing - review & editing. **Zi-Bing Yu:** Investigation. **Fei-Ran Shen:** Visualization. **Hou-Bo Zhou:** Investigation. **Yi-Hong Gao:** Investigation. **Kai-Ming Qiao:** Investigation. **Wen-Hui Liang:** Investigation. **Jia Li:** Investigation. **Cheng Zhang:** Investigation. **Jing Wang:** Formal analysis, Investigation. **Jun He:** Investigation. **Ji-Rong Sun:** Supervision. **Bao-Gen Shen:** Supervision.

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.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (Grant Nos. 2017YFB0702702, 2019YFA0704904, 2018YFA0305704, 2017YFA0206300, 2017YFA0303601, and 2016YFB0700903), the National Natural Science Foundation of China (Grant Nos. U1832219, 51531008, 51771223, 51590880, 51971240, 11674378, 11934016, 11921004), and the Key Program and Strategic Priority Research Program (B) of the Chinese Academy of Sciences.

References

- [1] K.A. Gschneidner, V.K. Pecharsky, Magnetic refrigeration materials (invited), *J. Appl. Phys.* 85 (1999) 5365–5368.
- [2] V. Franco, J.S. Blázquez, J.J. Ipus, J.Y. Law, L.M. Moreno-Ramírez, A. Conde, Magnetocaloric effect: From materials research to refrigeration devices, *Prog. Mater. Sci.* 93 (2018) 112–232.
- [3] B.G. Shen, J.R. Sun, F.X. Hu, H.W. Zhang, Z.H. Cheng, Recent Progress in Exploring Magnetocaloric Materials, *Adv. Mater.* 21 (2009) 4545–4564.
- [4] Y. Taguchi, H. Sakai, D. Choudhury, Magnetocaloric Materials with Multiple Instabilities *Adv. Mater.* 29 (2017) 1606144-1606144.
- [5] B. Li, W.J. Ren, Q. Zhang, X.K. Lv, X.G. Liu, H. Meng, J. Li, D. Li, Z.D. Zhang, Magnetostructural coupling and magnetocaloric effect in Ni–Mn–In, *Appl. Phys. Lett.* 95 (2009) 172506.
- [6] G.J. Liu, J.R. Sun, J. Lin, Y.W. Xie, T.Y. Zhao, H.W. Zhang, B.G. Shen, Entropy changes due to the first-order phase transition in the Gd₅Si₄Ge_{4-x} system, *Appl. Phys. Lett.* 88 (2006) 212505.
- [7] K.A. Gschneidner, Y. Mudryk, V.K. Pecharsky, On the nature of the magnetocaloric effect of the first-order magnetostructural transition, *Scripta Mater.* 67 (2012) 572–577.
- [8] V.K. Pecharsky, Giant Magnetocaloric Effect in Gd₅(Si₂Ge₂), *Phys. Rev. Lett.* 78 (1997) 4494–4498.
- [9] K.A. Gschneidner, V.K. Pecharsky Jr., Phase relationships and crystallography in the pseudobinary system Gd₅Si₄-Gd₅Ge₄, *J. Alloys Compd.* (1997) 98-106.
- [10] F.X. Hu, B.G. Shen, J.R. Sun, Z.H. Cheng, G.H. Rao, X.X. Zhang, Influence of negative lattice expansion and metamagnetic transition on magnetic entropy change in the compound LaFe_{11.4}Si_{1.6}, *Appl. Phys. Lett.* 78 (2001) 3675–3677.
- [11] A. Fujita, K. Fukamichi, J.T. Wang, Y. Kawazoe, Large magnetovolume effects and band structure of itinerant-electron metamagnetic La(Fe_xSi_{1-x})₁₃ compounds, *Phys. Rev. B* 68 (2003) 104431.
- [12] H. Wada, Y. Tanabe, Giant magnetocaloric effect of MnAs_{1-x}Sb_x, *Appl. Phys. Lett.* 79 (2001) 3302–3304.
- [13] H. Wada, S. Matsuo, A. Mitsuda, Pressure dependence of magnetic entropy change and magnetic transition in MnAs_{1-x}Sb_x, *Phys. Rev. B* 79 (2009) 092407.
- [14] S.C. Ma, D. Hou, F. Yang, Y.L. Huang, G. Song, Z.C. Zhong, D.H. Wang, Y.W. Du, The antiferromagnetic-ferromagnetic conversion and magnetostructural transformation in Mn-Ni-Fe-Ge ribbons, *Appl. Phys. Lett.* 104 (2014) 202412.
- [15] N.T. Trung, V. Biharie, L. Zhang, L. Caron, K.H.J. Buschow, E. Brück, From single- to double-first-order magnetic phase transition in magnetocaloric Mn_{1-x}Cr_xCoGe compounds, *Appl. Phys. Lett.* 96 (2010) 162507.
- [16] E.K. Liu, W.H. Wang, L. Feng, W. Zhu, G.J. Li, J.L. Chen, H.W. Zhang, G.H. Wu, C.B. Jiang, H.B. Xu, F. de Boer, Stable magnetostructural coupling with tunable magnetoresponsive effects in hexagonal ferromagnets, *Nat Commun.* 3 (2012) 873.
- [17] Y.Y. Zhao, F.X. Hu, L.F. Bao, J. Wang, H. Wu, Q.Z. Huang, R.R. Wu, Y. Liu, F.R. Shen, H. Kuang, M. Zhang, W.L. Zuo, X.Q. Zheng, J.R. Sun, B.G. Shen, Giant negative thermal expansion in bonded MnCoGe-based compounds with Ni₂In-type hexagonal structure, *J. Am. Chem. Soc.* 137 (2015) 1746–1749.
- [18] F.X. Hu, J. Gao, X.L. Qian, M. Ilyn, A.M. Tishin, J.R. Sun, B.G. Shen, Magnetocaloric effect in itinerant electron metamagnetic systems La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}, *J. Appl. Phys.* 97 (2005) 10M303.
- [19] V. Johnson, Diffusionless orthorhombic to hexagonal transitions in ternary silicides and germanides, *Inorg. Chem.* 14 (1975) 1117–1120.
- [20] S. Anzai, K. Ozawa, Coupled nature of magnetic and structural transition in MnNiGe under pressure, *Phys. Rev. B* 18 (1978) 2173–2178.
- [21] L. Jia, G.J. Liu, J.R. Sun, H.W. Zhang, F.X. Hu, C. Dong, G.H. Rao, B.G. Shen, Entropy changes associated with the first-order magnetic transition in LaFe_{13-x}Si_x, *J. Appl. Phys.* 100 (2006) 123904.
- [22] M.E. Gruner, W. Keune, B. Roldan Cuenya, C. Weis, J. Landers, S.I. Makarov, D. Klar, M.Y. Hu, E.E. Alp, J. Zhao, M. Krautz, O. Gutfleisch, H. Wende, Element-Resolved Thermodynamics of Magnetocaloric LaFe_{13-x}Si_x, *Phys. Rev. Lett.* 114 (2015) 024417.
- [23] J. Landers, S. Salamon, W. Keune, M.E. Gruner, M. Krautz, J. Zhao, M.Y. Hu, T.S. Toellner, E.E. Alp, O. Gutfleisch, H. Wende, Determining the vibrational entropy change in the giant magnetocaloric material LaFe_{11.6}Si_{1.4} by nuclear resonant inelastic x-ray scattering, *Phys. Rev. B* 98 (2018) 057202.
- [24] J. Lazewski, P. Piekarczyk, J. Tobola, B. Wiendlocha, P.T. Jochym, M. Sternik, K. Parlinski, Phonon mechanism of the magnetostructural phase transition in MnAs, *Phys. Rev. Lett.* 104 (2010) 147205.
- [25] L. Caron, N.T. Trung, E. Brück, Pressure-tuned magnetocaloric effect in Mn_{0.93}Cr_{0.07}CoGe, *Phys. Rev. B* 84 (2011) 020414(R).
- [26] N.T. Trung, L. Zhang, L. Caron, K.H.J. Buschow, E. Brück, Giant magnetocaloric

- effects by tailoring the phase transitions, *Appl. Phys. Lett.* 96 (2010) 172504.
- [27] R.R. Wu, L.F. Bao, F.X. Hu, H. Wu, Q.Z. Huang, J. Wang, X.L. Dong, G.N. Li, J.R. Sun, F.R. Shen, T.Y. Zhao, X.Q. Zheng, L.C. Wang, Y. Liu, W.L. Zuo, Y.Y. Zhao, M. Zhang, X.C. Wang, C.Q. Jin, G.H. Rao, X.F. Han, B.G. Shen, Giant barocaloric effect in hexagonal Ni_2In -type Mn-Co-Ge-In compounds around room temperature, *Sci. Rep.* 5 (2015) 18027.
- [28] A. Aznar, P. Lloveras, J.Y. Kim, E. Stern-Taulats, M. Barrio, J.L. Tamarit, C.F. Sanchez-Valdes, J.L. Sanchez Llamazares, N.D. Mathur, X. Moya, Giant and Reversible Inverse Barocaloric Effects near Room Temperature in Ferromagnetic $\text{MnCoGeB}_{0.03}$, *Adv. Mater.* 31 (2019) e1903577.
- [29] A.S.W. Baela, J. Todorovi, A. Zifba, Crystal and Magnetic Structure of the $\text{NiMnGe}_{1-x}\text{Si}_x$ System, *Phys. Stat. Sol* 64 (1981) 367–378.
- [30] S. Niziol, A. Weselucha, W. Bazela, A. Szytula, Magnetic-Properties of the $\text{Co}_x\text{Ni}_{1-x}\text{MnGe}$ System, *Solid State Commun.* 39 (1981) 1081–1085.
- [31] L.F. Bao, F.X. Hu, R.R. Wu, J. Wang, L. Chen, J.R. Sun, B.G. Shen, L. Li, B. Zhang, X.X. Zhang, Evolution of magnetostructural transition and magnetocaloric effect with Al doping in $\text{MnCoGe}_{1-x}\text{Al}_x$ compounds, *J. Phys. D: Appl. Phys.* 47 (2014) 055003.
- [32] F.X. Hu, B.G. Shen, J.R. Sun, X.X. Zhang, Great magnetic entropy change in $\text{La}(\text{Fe}, \text{M})_{13}$ ($\text{M} = \text{Si}, \text{Al}$) with Co doping, *Chin. Phys.* 09 (2000) 550–554.
- [33] A. Fujita, S. Fujieda, Y. Hasegawa, K. Fukamichi, Itinerant-electron metamagnetic transition and large magnetocaloric effects in $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ compounds and their hydrides, *Phys. Rev. B* 67 (2003) 104416.
- [34] J. Rosén, G. Grimvall, Anharmonic lattice vibrations in simple metals, *Phys. Rev. B* 27 (1983) 7199–7208.
- [35] P.J.v. Ranke, N.A. de Oliveira, C. Mello, A.M.G. Carvalho, S. Gama, Analytical model to understand the colossal magnetocaloric effect, *Phys. Rev. B*, 71 (2005) 054410.
- [36] J.Z. Hao, et al., Large enhancement of magnetocaloric and barocaloric effect by hydrostatic pressure in $\text{La}(\text{Fe}_{0.92}\text{Co}_{0.08})_{11.9}\text{Si}_{1.1}$ with NaZn_{13} -type structure, *Chem. Mater.* 32 (2020) 1807–1818.