Spontaneous generation of voltage in the magnetocaloric compound $La(Fe_{0.88}Si_{0.12})_{13}$ and comparison to $SmMn_2Ge_2$

M. Zou,[1,*] J. A. Sampaio,[1,†] V. K. Pecharsky,[1,2] and K. A. Gschneidner, Jr.[1,2]
[1]*The Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011-3020, USA*
[2]*Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-2300, USA*
(Received 28 August 2009; revised manuscript received 16 October 2009; published 17 November 2009)

Relationships among spontaneous generation of voltage (SGV), magnetocaloric effect, temperature induced first-order magnetic phase transformation, and its thermal effect have been studied based on experimental results of $La(Fe_{0.88}Si_{0.12})_{13}$ and $SmMn_2Ge_2$ compounds. Remarkable differences in magnetocaloric effects and temperature-induced unit-cell volume changes during their first-order magnetic phase transformations lead to dramatic differences in their SGV effects. Both temperature and magnetic field trigger SGV in $La(Fe_{0.88}Si_{0.12})_{13}$ compound, but no SGV has been observed in $SmMn_2Ge_2$. Our results clarify that it is not the first-order crystallographic or magnetic phase transformation per se, but the strong thermal effects, i.e., latent heat and magnetocaloric effect that play the key role in the SGV mechanism.

DOI: 10.1103/PhysRevB.80.172403 PACS number(s): 72.90.+y, 75.30.Kz, 75.30.Sg, 75.50.Bb

I. INTRODUCTION

The spontaneous generation of voltage (SGV) was discovered recently in $Gd_5(Si_xGe_{1-x})_4$ compounds.[1,2] It may lead to development of multifunctional miniature sensors that respond to changes in temperature, magnetic field, pressure, and their rates of change. The SGV occurs in the vicinity of first-order coupled magnetic and crystallographic phase transformations, which are also responsible for other interesting physical properties, such as the giant magnetocaloric effect, colossal magnetostriction, and giant magnetoresistance.[3] Other materials, such as FeS,[4] TiNi,[5] FeNi,[6] Ce,[7] and CuBr,[8] also display phenomena similar to SGV, although the authors have given different names to the effects. First-order crystallographic phase transformations (but without magnetic phase transitions) have been associated with the SGV in these materials.[4–8] Accordingly, one may relate the origin of SGV to first-order crystallographic phase transformations. Three different mechanisms of SGV have been suggested. They are the diffusion current model,[4] the motion of twin boundaries,[5] and the Seebeck effect,[6–8] i.e., the thermoelectric power. In the $Gd_5(Si_xGe_{1-x})_4$ system, the mechanism was believed to be the Seebeck effect.[1]

It is well known that the Seebeck voltage can be observed only when there is a temperature gradient between two ends of a specimen, to which the electrical connections have been made. In $Gd_5(Si_xGe_{1-x})_4$ system, this temperature gradient comes from heat absorption or emission during a nonequilibrium process of the first-order magnetostructural transformation.[1,2] The origin of this heat absorption or emission, however, has not been clarified.[1,2] It has been reported that the crystallographic phase transformation at T_C involves a large ($\sim$1%) unit-cell volume change. By rearranging the Clausius-Clapeyron equation[9] $\frac{dP}{dT}=\frac{\Delta S}{\Delta V}=\frac{\Delta E}{T\Delta V}$ to $\Delta E=T\frac{dP}{dT}\Delta V$, where P, T, S, V, and E are the pressure, temperature, entropy, volume, and enthalpy, respectively, one obtains that the volume change (ΔV) is proportional to the enthalpy change (ΔE), i.e., to the latent heat of a first-order phase transformation. Thus, the large unit-cell volume change in $Gd_5(Si_xGe_{1-x})_4$ indicates a substantial latent heat. The magnetic-field-induced SGV in $Gd_5(Si_xGe_{1-x})_4$ occurs simultaneously with the giant magnetocaloric effect, which is a measurable adiabatic temperature change (ΔT_{ad}), or equivalently, a large isothermal magnetic entropy change (ΔS_M) near its Curie temperature (T_C). Thus, the latent heat and the magnetocaloric effect may be the source of the temperature gradient necessary for the occurrence of SGV, but not the change in the crystal structure per se.

To test this hypothesis, it is necessary to study SGV behaviors in systems possessing first-order phase transformations involving large magnetocaloric effect but without crystallographic symmetry change. The $La(Fe_{0.88}Si_{0.12})_{13}$ compound is such a material. It is ferromagnetic below its T_C of 195 K.[10] The first-order magnetic transition at T_C is accompanied by a large discontinuous volume change ($\sim$1%), but the system remains cubic without changing symmetry.[10] The isothermal magnetic entropy change ΔS_M estimated by the Maxwell relation, $(\partial S_M/\partial H)_T=(\partial M/\partial T)_H$, (where S_M, H, M, and T are magnetic entropy, magnetic field, magnetization, and temperature, respectively), is about -18 J/kg K at T_C in the field change in 10 kOe.[11] The giant magnetocaloric effect of $La(Fe_{0.88}Si_{0.12})_{13}$ is related to the itinerant-electron metamagnetic (IEM) transition, i.e., a magnetic-field-induced first-order magnetic transition from Pauli paramagnetic to itinerant-electron ferromagnetic state above its T_C.[11]

To further define the role of the thermal effect (latent heat and magnetocaloric effect) in SGV, the $SmMn_2Ge_2$ compound is studied because it also exhibits first-order magnetic phase transformations without crystallographic phase change. The volume change and magnetocaloric effect during these transformations, however, are much smaller than those in $La(Fe_{0.88}Si_{0.12})_{13}$.[12,13] Given that the volume change is proportional to the latent heat of a first-order phase transformation, a comparison of the SGV behaviors of $SmMn_2Ge_2$ and $La(Fe_{0.88}Si_{0.12})_{13}$ may shed light on the relationship between SGV and latent heat.

The re-entrant ferromagnet $SmMn_2Ge_2$ crystallizes in a body-centered tetragonal structure. It exhibits two first-order magnetic transitions between ferromagnetic and antiferromagnetic states, at $\sim$106.5 K, (T_1) and $\sim$153 K, (T_2).[12] Its

TABLE I. The nature, lattice parameter changes, and magnetocaloric effects of magnetic phase transitions of $Gd_5Si_2Ge_2$, $SmMn_2Ge_2$, and $La(Fe_{0.88}Si_{0.12})_{13}$ compounds.

	$Gd_5Si_2Ge_2$	$SmMn_2Ge_2$	$La(Fe_{0.88}Si_{0.12})_{13}$
	Refs. 3 and 14	Refs. 12 and 13	Refs. 10 and 11
Nature of magnetic phase transition	First order	First order	First order
Coupled crystallographic phase transition?	Yes	No	No
Unit cell volume change during the phase transformation ($\Delta V/V$)	1%	0.3%	1%
$-\Delta S_M$ for $\Delta H=10$ kOe (J/kg K)	12	1.4	18

magnetic order-disorder transition at T_C (~350 K) is of second order.[12] During the two first-order magnetic transformations, the lattice parameter a changes by ~0.2%. The c parameter changes only by ~0.02% at T_1 and ~0.06% at T_2. The resulting volume changes are ~0.25% at T_1 and ~0.3% at T_2.[12] The entropy changes calculated using Clausius-Clapeyron's equation are −0.8 J/kg K at T_1 and 1.1 J/kg K at T_2.[13] The magnetic entropy changes ΔS_M estimated through the Maxwell relation are 1.3 J/kg K at T_1, and −1.4 J/kg K at T_2 for a magnetic field change in 10 kOe.[13] The change in lattice parameters and unit-cell volume, and the magnetocaloric effect during the first-order phase transformation in $SmMn_2Ge_2$ are also much smaller than those in $Gd_5(Si_xGe_{1-x})_4$.[3,14] Table I lists the comparison of the nature of phase transitions, unit-cell volume changes during phase transformations, and magnetocaloric effects of $Gd_5Si_2Ge_2$, $SmMn_2Ge_2$, and $La(Fe_{0.88}Si_{0.12})_{13}$ compounds.

II. EXPERIMENTAL DETAILS

Polycrystalline $La(Fe_{0.88}Si_{0.12})_{13}$ was prepared by arc-melting a stoichiometric mixture of the constituent materials under an argon atmosphere. The button was flipped and remelted several times to ensure the compositional homogeneity. The La, Fe, and Si were purchased from commercial vendors, and were 99.9, 99.95, and 99.9995 wt. % pure, respectively. The arc-melted alloy was then heat treated for 10 days at 1320 K in an evacuated quartz tube back-filled with helium. The x-ray powder diffraction patterns showed that the specimen crystallizes in the $NaZn_{13}$-type cubic structure with ~7 wt. % of α-Fe impurity phase. A rectangular parallelepiped-shaped sample with dimensions of $1.3\times1.3\times5.8$ mm^3 was then cut using a low speed diamond saw. The $SmMn_2Ge_2$ sample is a single crystal shaped as a thin plate with dimensions of $2.2\times2.4\times0.2$ mm^3. The ab plane of the unit cell was parallel to the thin plate.

Electrical connections were made by attaching the thin platinum wires to both ends of each sample using silver epoxy (EPO-TEKH20E) manufactured by Epoxy Technology, Inc. The contact resistances were between 1 to 2 ohms. The SGV measuring method, instrument set up, and experiment errors were described elsewhere.[2]

The dc magnetization (M) as a function of temperature (T) and magnetic field (H) was measured by using a superconducting quantum interference device (SQUID) magnetometer, MPMS-XL from Quantum Design, Inc. The magnetic fields were varied between 0 and 40 kOe with a 2 kOe step. The magnetocaloric effect, $-\Delta S_M$, was evaluated from the $M(H)$ data according to the Maxwell relation $(\partial S_M/\partial H)_T = (\partial M/\partial T)_H$.

III. RESULTS AND DISCUSSION

For $SmMn_2Ge_2$, no SGV signal is triggered either by temperature or magnetic field near 106.5 and 153 K, where both first-order magnetic phase transformations occur, as shown in Fig. 1. Recall that the volume change and the magnetocaloric effect during these transformations in $SmMn_2Ge_2$ are much smaller than those of $Gd_5(Si_xGe_{1-x})_4$, the absence of SGV in $SmMn_2Ge_2$, therefore, supports the correlation of SGV with latent heat and magnetocaloric effect.

On the other hand, the SGV is strong and easily measurable in the $La(Fe_{0.88}Si_{0.12})_{13}$ compound. The SGV as a function of temperature measured in a zero magnetic field upon heating at ~1 and ~3 K/min, and cooling at ~1 and

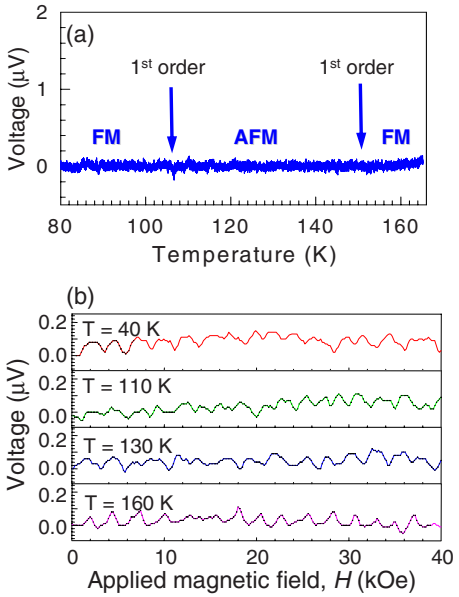

FIG. 1. (Color online) Voltage signals of $SmMn_2Ge_2$ for temperature (a) and magnetic field (b) changes. The rates of change in temperature and magnetic field were 3 K/min and 40 kOe/min, respectively.

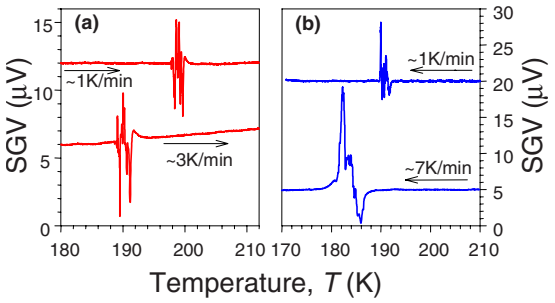

FIG. 2. (Color online) The SGV of $La(Fe_{0.88}Si_{0.12})_{13}$ as a function of temperature measured upon heating at ~1 and ~3 K/min (a) and upon cooling at ~1 and ~7 K/min (b) in a zero magnetic field.

~7 K/min is shown in Fig. 2. The SGV signals are essentially S shape, similar to those observed in $Gd_5(Si_xGe_{1-x})_4$.[1,2] The magnitudes of SGV signals increase with increasing temperature change rate, in accordance with the observation in $Gd_5Si_2Ge_2$.[2]

Figure 2 shows that the SGV of $La(Fe_{0.88}Si_{0.12})_{13}$ on cooling at 1 K/min starts to appear at 194 ± 2 K, which is very close to the T_C of 194 K. The T_C is estimated as the temperature where $|dM/dT|$ has a maximum value. The $M(T)$ data are not shown here. Recall that the volume change[10] ($\Delta V/V \sim 1\%$) of the first-order magnetic phase transformation in $La(Fe_{0.88}Si_{0.12})_{13}$ at T_C is comparable to that of $Gd_5(Si_xGe_{1-x})_4$ (Ref. 3), and $\Delta V/V$ is proportional to the latent heat (see above). The proximity of the start temperature of SGV and T_C supports that the temperature induced SGV is closely related to the latent heat.

The SGV of $La(Fe_{0.88}Si_{0.12})_{13}$ as a function of magnetic field measured isothermally in the vicinity of T_C upon field increasing and decreasing at ~40 kOe/min are shown in panels (a) and (b), respectively, of Fig. 3. Panel (c) displays the magnetization isotherms for the same sample. Panel (d) shows a magnetic phase diagram constructed based on the magnetization isotherm data upon field increasing. From panels (a), (b), and (c), one can see that the SGV and IEM transition (within the field limit of 40 kOe) start and end at the same temperatures, which are ~194 and ~212 K, respectively. In addition, the SGV peaks are located close to the phase boundaries of IEM phase transitions upon field increasing, as shown in panel (d). The close relationship between the SGV peak positions and IEM phase boundaries is preserved in the field decreasing data. For clarity they are not shown here. Since the IEM transition is accompanied by the giant magnetocaloric effect, these observations support the correlation between the magnetic field induced SGV and the giant magnetocaloric effect.

Panels (a), (b), and (c) of Fig. 3 also illustrate that both the magnitude of SGV and the change in magnetization upon IEM transition are suppressed as temperature increases further above T_C. According to the Maxwell relation $(\partial S_M/\partial H)_T = (\partial M/\partial T)_H$, the change in magnetization is proportional to the magnetic entropy change [as follows from Fig. 3(d), $\partial H/\partial T$ remains nearly constant between 0 and 40 kOe], i.e., is proportional to the magnetocaloric effect. To further clarify the role of the giant magnetocaloric effect of

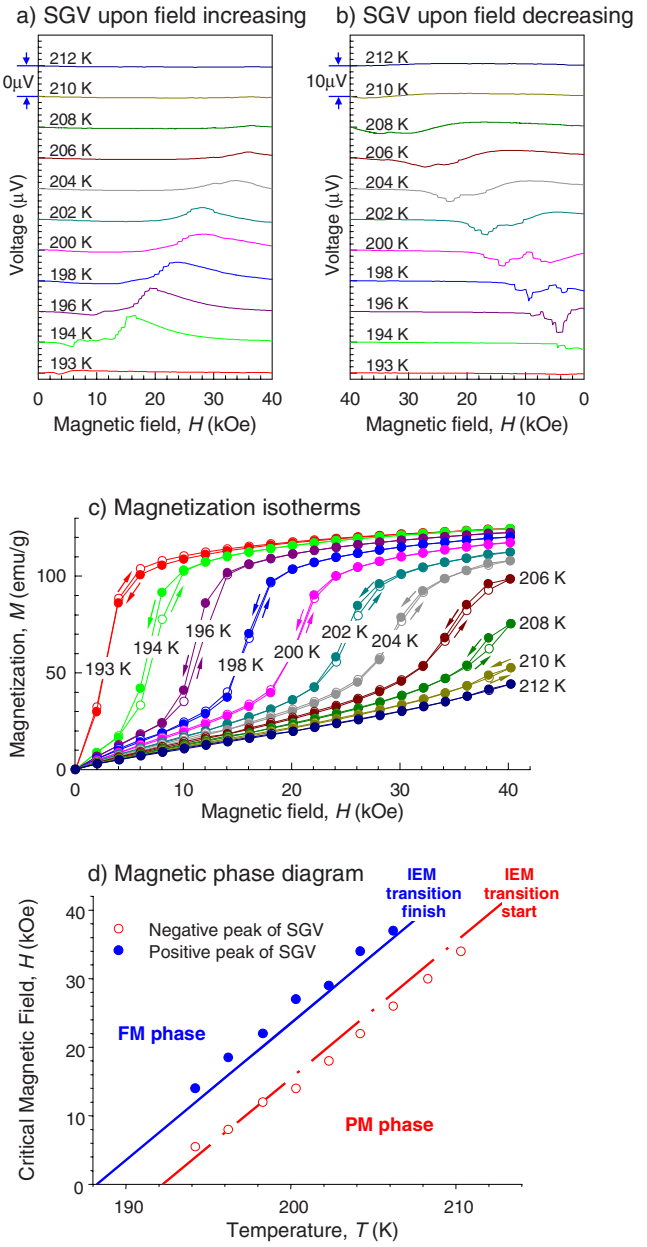

FIG. 3. (Color online) The SGV of $La(Fe_{0.88}Si_{0.12})_{13}$ triggered isothermally by increasing (a) and decreasing (b) magnetic field at a rate of 40 kOe/min at temperatures near T_C; magnetization isotherms measured at corresponding temperatures (c); and magnetic phase diagram (d) constructed based on the data of panel (a) and field increasing data of panel (c).

$La(Fe_{0.88}Si_{0.12})_{13}$ in SGV, the magnitude of SGV (the vertical distance between the positive and negative peaks) and $-\Delta S_M$ as functions of temperature are plotted together in Fig. 4. Clearly, the magnitude of the SGV follows that of the magnetocaloric effect. Because the magnitude of the Seebeck voltage is proportional to the temperature gradient (ΔT) between two ends of a sample, the correspondence of the magnitudes of SGV and ΔS_M seen in Fig. 4 strongly supports the notion that the magnetocaloric effect determines the magnitude of SGV by determining ΔT.

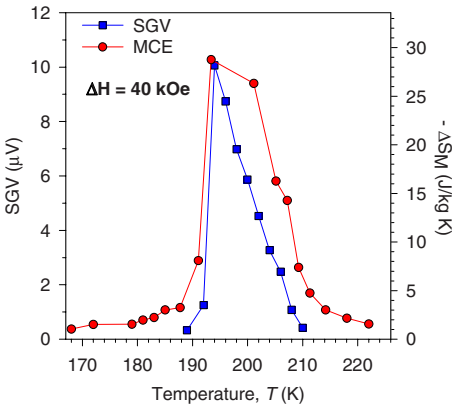

FIG. 4. (Color online) The SGV (squares) and magnetocaloric effect (MCE) (circles) of $La(Fe_{0.88}Si_{0.12})_{13}$ as functions of temperature near T_C for a 40 kOe magnetic field change.

IV. CONCLUSIONS

In conclusion, the key factor in SGV mechanism has been studied based on the SGV behaviors of two intermetallic compounds, $La(Fe_{0.88}Si_{0.12})_{13}$ and $SmMn_2Ge_2$. Although both of them exhibit first-order magnetic phase transformations, the change in the unit-cell volume (and therefore, the latent heat) and the magnetocaloric effect of the two compounds are vastly different. The SGV signals can be triggered by changing temperature and/or magnetic field in $La(Fe_{0.88}Si_{0.12})_{13}$, which has much greater unit-cell volume change and magnetocaloric effect than $SmMn_2Ge_2$. In $SmMn_2Ge_2$, no SGV can be triggered by the same stimuli. The dramatically different SGV behaviors of the two compounds indicate that neither the first-order crystallographic nor the magnetic phase transformation is the prerequisite for SGV. The strong thermal effect (latent heat or magnetocaloric effect) is the key for triggering SGV.

ACKNOWLEDGMENTS

The authors thank Paul C. Canfield for providing $SmMn_2Ge_2$ samples. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences. The Ames Laboratory is operated for the U.S. DOE by Iowa State University under Contract No. DE-AC02-07CH11358.

*Corresponding author; zoumin@iastate.edu
†Present address: Laboratório de Ciências Físicas, Universidade Estadual do Norte Fluminense, Av. Alberto Lamego 2000, Campos dos Goytacazes 28015-620, Rio de Janeiro, Brazil.

[1] E. M. Levin, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **63**, 174110 (2001).
[2] M. Zou, H. Tang, D. L. Schlagel, T. A. Lograsso, K. A. Gschneidner, Jr., and V. K. Pecharsky, J. Appl. Phys. **99**, 08B304 (2006).
[3] V. K. Pecharsky and K. A. Gschneidner, Jr., Pure Appl. Chem. **79**, 1383 (2007) and references therein.
[4] T. Takahashi and O. J. Yamada, J. Phys. Chem. Solids **37**, 161 (1976).
[5] A. D. Johnson and P. I. Katz, J. Appl. Phys. **48**, 73 (1977).
[6] Yu. N. Koval and A. L. Molin, Fiz. Met. Metalloved. **49**, 1099 (1980).
[7] V. V. Kokorin and V. A. Chernenko, Fiz. Met. Metalloved. **60**, 285 (1985).
[8] I. Riess, R. Safadi, E. Zilberstin, and H. L. Tuller, J. Appl. Phys. **69**, 1205 (1991).
[9] M. W. Zemansky and R. H. Dittman, *Heat and Thermodynamics*, 7th ed. (McGraw-Hill, New York, 1997).
[10] A. Fujita, S. Fujieda, K. Fukamichi, H. Mitamura, and T. Goto, Phys. Rev. B **65**, 014410 (2001).
[11] S. Fujieda, A. Fujita, and K. Fukamichi, Appl. Phys. Lett. **81**, 1276 (2002).
[12] M. Duraj, R. Duraj, A. Szytula, and Z. Tomkowicz, J. Magn. Magn. Mater. **73**, 240 (1988).
[13] K. Koyama, S. Miura, H. Okada, T. Shigeoka, S. Fujieda, A. Fujita, K. Fukamichi, and K. Watanabe, J. Alloys Compd. **408-412**, 118 (2006).
[14] A. O. Pecharsky, K. A. Gschneidner, Jr., and V. K. Pecharsky, J. Appl. Phys. **93**, 4722 (2003).