Determination of the entropy changes in the compounds with a first-order magnetic transition

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Entropy changes in the compounds of $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ (x=0.3 and 0.4) have been experimentally studied. A tower-shaped entropy change of the height of ~27 J/kg K is obtained based on the analyses of heat capacity, while the Maxwell relation predicts an extra entropy peak of the height of ~99 J/kg K, slightly varying with Pr content. A careful study indicates that the Maxwell relation cannot be used in the vicinity of the Curie temperature because of the coexistence of paramagnetic and ferromagnetic phases, and the huge entropy peak is a spurious result. Similar conclusions are applicable to MnAs and $Mn_{1-x}Fe_xAs$, for which huge entropy changes have been reported. Appropriate methods for the determination of entropy change of the compound with phase separation are discussed based on the magnetic data. © *2007 American Institute of Physics*.
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Much effort has been devoted to the exploration of potential magnetocaloric materials since the discovery of giant entropy changes in $Gd_5Si_2Ge_2$,[1] $MnAs_{1-x}Sb_x$,[2] $MnFeP_{1-x}As_x$,[3] and $LaFe_{13-x}Si_x$,[4] which demonstrates the possibility to apply the magnetic refrigeration technique under the ambient conditions. The maximum entropy change (ΔS) is ~32 J/kg K for a field change of 0–5 T under the ambient condition, observed in $MnAs_{1-x}Sb_x$. Although this value is significantly larger than that of the ordinary material, it still cannot meet the demands of practical application. The most striking recent discovery is the great enhancement of the entropy change under pressures. Gama *et al.*[5] found that the entropy change of MnAs can be as high as ~267 J/kg K for a field change of 0–5 T in the presence of a constant pressure of 0.23 GPa, which is a value much larger than the theoretical result (~103 J/kg K). By partially replacing Mn with Fe, de Campos *et al.*[6] further obtained an entropy change of ~320 J/kg K under the ambient pressure. Pressure-enhanced entropy change was also observed in the $LaFe_{13-x}Si_x$ intermetallics.[7] The entropy change exhibits as a ΔS spike of the height of ~60 J/kg K followed a flat plateau. There are also reports that rare-earth-doping produces similar effects as pressure, and a ΔS spike of the height of ~70 J/kg K was observed in $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$.[8] Based on a phenomenological model, von Ranke *et al.*[9] presented an explanation to the huge magnetocaloric effect (MCE) in MnAs, and it was believed that lattice entropy made a great contribution to ΔS. These results, if confirmed, are very important in the sense that they depict a bright prospect for the application of the magnetic cooling technique.

We noted that the entropy changes above mentioned were calculated by the Maxwell relation, and there is no evidence from calorimetric data, the latter is no doubt necessary to confirm the occurrence of the extraordinary MCE. In this letter we performed a systematic study on Pr-doped $LaFe_{11.5}Si_{1.5}$ intermetallics, based on both the magnetic and calorimetric measurements. Although the analyses of the Maxwell relation give similar results as those previously reported, entropy changes obtained from heat capacity indicate the absence of the huge ΔS spike. Further study indicates that the Maxwell relation cannot be used in the vicinity of the Curie temperature because of the coexistence of paramagnetic (PM) and ferromagnetic (FM) phases, and the huge entropy peak is a spurious result. Proper methods for the determination of entropy change based on the magnetic data are discussed.

Two polycrystalline samples with the nominal composition $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ for x=0.3 and 0.4 were prepared by arc melting appropriate amounts of starting materials (99.9% in purity) under ultrapure argon atmosphere (~10 at. % excessive La and Pr were used to compensate the weight loss during the arc melting). The resultant ingots were annealed in an evacuated quartz tube at 1050 °C for one month, to improve the crystallization of the sample, then quenched into liquid nitrogen. Phase purity and crystal structure of the samples were studied by powder x-ray diffraction. It is proved that the present samples crystallized in the $NaZn_{13}$-type cubic structure, without secondary phases. The lattice parameter reduces from 11.468 to 11.453 Å for x=0.3 and to 11.448 Å for x=0.4.

Compared with $LaFe_{11.5}Si_{1.5}$, the introduction of Pr causes a reduction of the Curie temperature from ~193 to ~184 K (x=0.3) or ~181 K (x=0.4), which could be a re-

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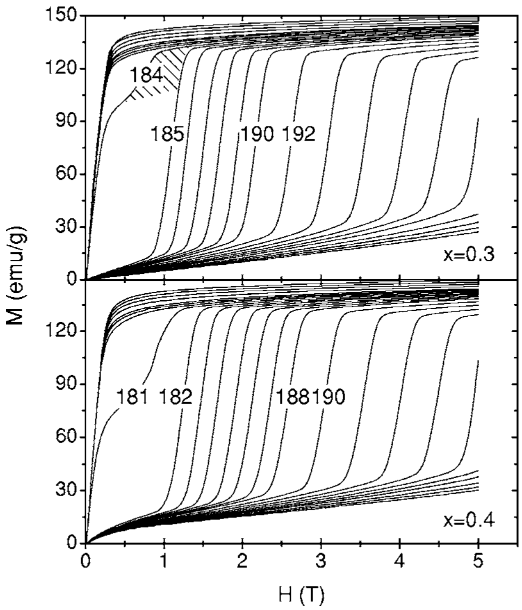

FIG. 1. Magnetization isotherms of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.6}Pr_{0.4}Fe_{11.5}Si_{1.5}$ measured in the field increase process. Hatched area marks the area that contributes to entropy change. Numbers in the figure indicate the temperature in units of kelvin.

sult of lattice shrinkage. Figure 1 shows the typical magnetization isotherms, $M(H)$, of $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ measured in the field increase process. Temperature steps of 1 K near T_C and 2 K far away from T_C were adopted for the measurements. The magnetization exhibits a stepwise behavior in the temperature range adjacent to T_C. It grows rapidly with applied field up to an intermediate height first, and subsequent increase in magnetic field has minor effect on magnetization until a critical field, after which a metamagnetic transition occurs. These features are especially obvious in the sample $x=0.4$. These behaviors actually indicate the coexistence of the PM and FM phases near and above T_C. Stepwise behaviors disappear at high temperatures, and only the steep metamagnetic transition survives.

Magnetic entropy change can be calculated based on the Maxwell relation $\Delta S_m(T,H)=\int_0^H(\partial M/\partial T)_H dH$. Figure 2 presents the entropy change as a function of temperature for a field change of 0–5 T. In addition to the flat ΔS_m plateau of the height of ~28 J/kg K, an extra spike-shaped peak of the

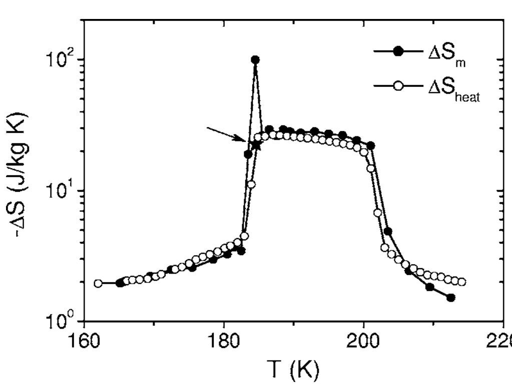

FIG. 2. Temperature-dependent entropy changes of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ calculated from magnetic data (solid circles) and heat capacity (open circles). The peak value drops from ~99 to ~22 J/kg K if only the contributions from the metamagnetic transition are considered (marked by an arrow). Δ has been set ~1.5 J/kg K. Solid lines are guides for the eyes.

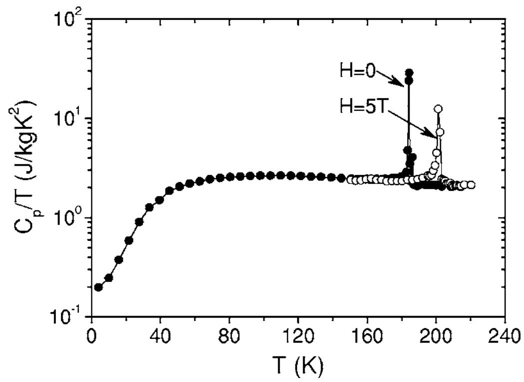

FIG. 3. Heat capacity of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ measured under the fields of $H=0$ and 5 T.

height of ~99.6 J/kg K (for $x=0.3$) or 92.6 J/kg K (for $x=0.4$) appears. It is interesting to note that the ΔS_m spike appears in exactly the same temperature range where the stepwise magnetic behaviors occur. We have tried to change the temperature steps of the magnetic measurements from 1 to 0.5 K, and essentially similar results are obtained except for a slight variation in peak height.

We noted that the ΔS_m spike exists in the results calculated by the Maxwell relation for a wide variety of materials such as $Gd_5Si_{4-x}Ge_x$ (Ref. 10) and $MnAs_{1-x}Sb_x$,[2] though the peak value is not as large as those observed here. It is therefore necessary to give a careful analysis on its origin, especially when the spike value can be as large as ~100 J/kg K. For a further investigation of the huge MCE, the heat capacity (C_p) of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ was measured. Considering the fact that only the difference of the heat capacities for $H=0$ and $H=5$ T is required for calculating ΔS_{heat}, and significant differences occur only near T_C, the heat capacity under the field of 5 T was measured in the temperature range from 150 to 220 K. In response to the magnetic transition, a C_p spike appears, as shown in Fig. 3, which indicates the typical first-order character of the phase transition. A field of 5 T causes an upward shift of the C_p peak by ~20 K, together with an obvious peak broadening.

Based on the formula $\Delta S_{heat}(T)=\Delta+\int_{150\ K}^{T}[C_p(5T)-C_p(0)]dT/T$, the entropy change can be calculated, where Δ is the entropy change at 150 K, and it is small.[11] As shown in Fig. 2, the entropy change exhibits as a flat plateau with a maximum height of ~26.8 J/kg K and a width of ~20 K. Noting that the ΔS_m plateau is ~28.3 J/kg K, the agreement between ΔS_m and ΔS_{heat} is satisfactory.

The most striking observation is the absence of the ΔS spike. This is a result in consistent with that of Pecharsky *et al.*,[11] who have shown that no ΔS spikes are expected for a normal first-order transition. These results imply that the huge entropy change predicted by the Maxwell relation could be spurious. It has been proved that the Clausius-Clapeyron equation is equivalent to the Maxwell relation for a first-order phase transition. However, in the case of the coexistence of the PM and FM phases, the entropy change should be handled carefully. Figure 4 is a schematic diagram showing the calculation of ΔS for the system with an idealized stepwise behavior. Denoting the area surrounded by the two M-H curves at T_1 and T_2 as $\Sigma_1+\Sigma_2$, the Maxwell relation gives $\Delta S[(T_1+T_2)/2]=(\Sigma_1+\Sigma_2)/(T_1-T_2)$. Considering the fact that the field-induced metamagnetic transition takes place in PM phase, however, only Σ_1 contributes to ΔS. This

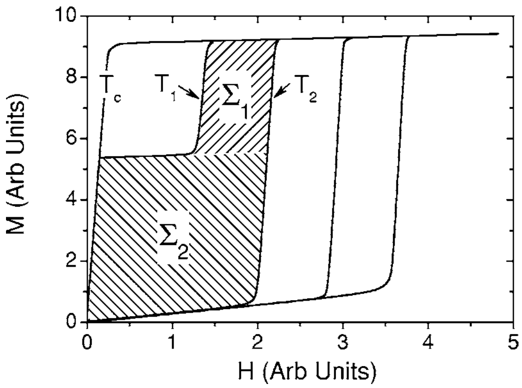

FIG. 4. Schematic diagram showing the calculation of entropy change when stepwise magnetic behaviors occur.

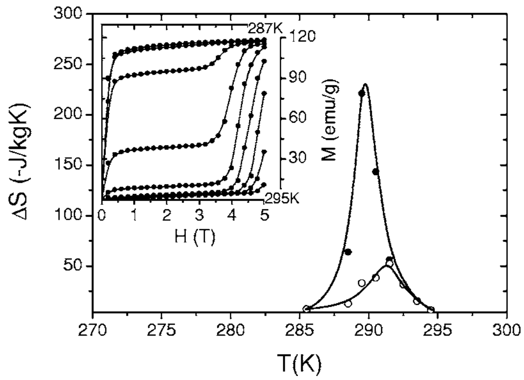

FIG. 5. Entropy changes of MnAs under a pressure of 0.18 GPa. Solid symbols represent the results calculated by the Maxwell relation, and open symbols are the contributions from the metamagnetic transition only. Inset plot shows the magnetization isotherms measured under the pressure of 0.18 GPa (Ref. 5).

implies that $\Delta S[(T_1+T_2)/2]=\Sigma_1/(T_1-T_2)$. Defining the volume fraction of the PM phase as $f(T)$, the above equation is equivalent to $\Delta S(T)=f(T)M\Delta H/\Delta T_C$. Based on this formula, ΔS_m of $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ was recalculated, and the results are shown in Fig. 2. As expected, the huge entropy peaks disappear. It is obvious that the huge ΔS spike is due to the inadequate inclusion of Σ_2 in the calculation.

As mentioned above, stepwise magnetic behavior exists in many materials such as MnAs and $Gd_5Si_{4-x}Ge_x$, especially in the former, which shows a huge entropy change near the Curie temperature. It is a natural question whether the huge MCE in MnAs is of the same origin. The MCE of MnAs cannot be verified by the measurement of heat capacity under pressure. However, occurrence of stepwise magnetic behaviors indicates the coexistence of two phases in MnAs in the temperature range near T_C. This suggests the inadequateness of the Maxwell relation to this compound. Based on a similar analysis, the entropy changes of MnAs under a pressure of 0.18 GPa are recalculated and the results are presented in Fig. 5. It is shown that the maximum entropy change is $\sim$52 J/kg K, appearing at $\sim$291 K, instead of the $\sim$220 J/kg K at 289.5 K. Compared with $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$, the ΔS_m spike in MnAs is much wider. The apparent reason for this is that the two phase coexistence occurs in a large temperature range in MnAs or, in other words, the magnetic transition in MnAs is much broader. Similar analyses can be performed for $Mn_{1-x}Fe_xAs$.

In summary, the entropy changes in the compounds $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ (x=0.3 and 0.4) have been experimentally studied. A tower-shaped entropy change of the height of $\sim$27 J/kg K is obtained by the analyses of heat capacity, while the Maxwell relation predicts an extra entropy peak of the height of $\sim$99 J/kg K, slightly varying with Pr content. A careful study indicates that the Maxwell relation cannot be used in the vicinity of the Curie temperature because of the coexistence of paramagnetic and ferromagnetic phases, and the huge entropy peak is a spurious result. Further analyses indicate that similar conclusions are applicable to MnAs and $Mn_{1-x}Fe_xAs$, for which huge entropy changes have been reported. Appropriate methods for the determination of entropy change of the compound with phase separation are discussed based on the magnetic data.

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