Comment on "Direct Measurement of the 'Giant' Adiabatic Temperature Change in $Gd_5Si_2Ge_2$"

In a recent paper [1], Giguère *et al.* argued that the Maxwell relation was not usable for $Gd_5Si_2Ge_2$, and, instead, a formula (Clausius-Clapeyron equation) that relates the magnetization jump at the transition and the shift of the critical point with magnetic field should be used. For $Gd_5Si_2Ge_2$, the maximum entropy change, estimated in this way, is 12.5 $J\,kg^{-1}\,K^{-1}$, ~26% lower than that predicted by the Maxwell relation. The adiabatic temperature change calculated from this ΔS value is ~10 K, in excellent agreement with the direct measurement result.

Magnetocaloric effect (MCE) associated with a first-order transition has received increasing attention in recent years due to its great potential for practical application. Fe-Rh [2] and Gd-Si-Ge [1,3] are typical intermetallics in which the MCE arises from a change of magnetic order when the system experiences a structure transition. The work of Giguère *et al.* involves the estimate of the entropy change in these types of materials. Considering the generality of this problem, a further study is warranted.

We now focus our attention on the effects from a first-order transition. In this case, magnetization (M) can be assumed temperature (T) independent in either phase the transition involves, which is an assumption equivalent to that made by Giguère *et al*. Then M is a step function of T with a jump of ΔM at Tc, the critical point. Based on the integrated Maxwell relation, entropy change can be expressed as

$$\begin{aligned}\Delta S &= -\int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right)_H dH \\ &= \int_{Tc(0)}^{Tc(H_{\max})} \Delta M\,\delta(T - Tc)\left(\frac{dTc}{dH}\right)^{-1} dTc \\ &= \frac{\Delta H \Delta M}{\Delta Tc}, \end{aligned} \tag{1}$$

where $H_{\max}$ represents the maximum magnetic field. The equalities $(\partial M/\partial T)_H = -\Delta M\,\delta(T - Tc)$ [4] and $dTc/dH = \Delta T/\Delta H$ were used during the derivation.

Equation (1) is the very formula obtained by Giguère *et al.,* and it indicates a constant entropy change in the temperature range from $Tc(0)$ to $Tc(H_{\max})$ while null otherwise, without the effects from the variation of the magnetic order parameter. These studies demonstrate that the Maxwell relation can be used for the calculation of entropy change accompanied by a first-order transition, at least in form, though its derivation requires that the thermodynamic potential be an exact differential.

In real material, a first-order transition takes place in a finite temperature region. During the transition, the magnetic order and magnetic order parameter may change simultaneously. Take $Gd_5Si_2Ge_2$ as an example. A first-order transition occurs at 270 K. Significant spin fluctuation exists near Tc, especially when the magnetic field drives the transition to higher temperatures (a shift of ~40 K can be produced by a field of 7 T), as demonstrated by the decrease of the magnetization with temperature and the reduction of the magnetization jump at $Tc(H)$ (Fig. 1 in [1]). Obviously, neglecting the effects from the suppression of spin fluctuation by an applied field may cause one to underestimate ΔS, as Giguère *et al.* [1] did, and the resulting errors could be ~26% as large. In this case, the Maxwell relation shows its obvious advantage over the Clausius-Clapeyron equation. It covers the effects from changes of both the magnetic order and the magnetic order parameter. In $Gd_5Si_2Ge_2$, the first-order transition takes place at ~272 K [1,3], which implies there would be no entropy change below 272 K according to the Clausius-Clapeyron equation. This directly conflicts with the fact that considerable adiabatic temperature change ($\Delta T_{ad} = 4$–6.5 K) was detected in a wide temperature range below 270 K (Fig. 3 in [1]). In contrast, the Maxwell relation gives $\Delta S \approx 10\ J\,kg^{-1}\,K^{-1}$ at 270 K, and a nonzero ΔS well below 270 K (Fig. 2 in [1]).

Alternatively, the adiabatic temperature change can also be determined indirectly via the data of ΔS and heat capacity. According to Giguère *et al.* [1], ΔT_{ad} is ~10 and 15 K, based on the ΔS of ~12.5 and 22.5 $J\,kg^{-1}\,K^{-1}$, calculated from the Clausius-Clapeyron formula and the Maxwell relation, respectively. The maximum entropy change by the Maxwell relation is, except for the spike value, ~18.6 $J\,kg^{-1}\,K^{-1}$ under a 7 T applied field. A spline extrapolation gives $\Delta T_{ad} \approx 13$ K. Taking into account the possible kinetic effects [5] that may cause an underestimate of the MCE in $Gd_5Si_2Ge_2$ [1] and the significant experimental errors of the direct (5%–10%) and indirect (3%–10%) measurement of the adiabatic temperature variation [6], this result is reasonable.

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J. R. Sun, F. X. Hu, and B. G. Shen
State Key Laboratory for Magnetism, Institute of Physics
and Center for Condensed Matter Physics
Chinese Academy of Sciences
Beijing 100080, People's Republic of China

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