The origin of large overestimation of the magnetic entropy changes calculated directly by Maxwell relation

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By investigating the nature of the first-order magnetostructural phase transition, we point out the origin of large overestimation of magnetic entropy changes calculated by directly applying the Maxwell relation. Furthermore, if the mass variations in ferromagnetic and paramagnetic phases on temperature are taken into consideration in two-phase region, taking MnAsC_x, (Mn, Al)As, and Mn_{0.994}Fe_{0.004}As compounds as example, based on the modified Maxwell relation, the large overestimation and discrepancy of magnetic entropy changes disappear. The magnetic entropy changes are equivalent with the values by Clausius–Claperyon equation, indicating the validity of this modified approach. © 2010 American Institute of Physics. [doi:10.1063/1.3446843]

Recently, for the purpose of reducing the greenhouse gases emissions, people are motivated to find magnetic materials with a large ambient magnetic entropy change (ΔS_M), which is based on the magnetocaloric effect (MCE).^{1–7} Since the discovery of Gd₅Si₂Ge₂-type compounds with giant MCE,¹ magnetic materials with the first-order magnetostructural phase transition (FOMPT) have attracted much attentions. Not soon later, arguments on both the nominal giant ΔS_M and the validity of the Maxwell relation in FOMPT also appeared.^{2–5} Generally, the Maxwell relation is written as follows:

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$$\Delta S_M(T, \Delta B) \approx \int_0^B \left(\frac{\partial M}{\partial T}\right) dB$$
$$= \frac{1}{\Delta T} \left(\int_0^B M_{i+1}(B) dB - \int_0^B M_i(B) dB\right). \quad (1)$$

Here, $\Delta T = T_{i+1} - T_i \cdot M_{i+1}$ and M_i are the magnetization measured at two temperatures T_{i+1} and T_i . Using Eq. (1), 0.3% Fe-doped MnAs system underwent a FOMPT and showed a "colossal" ΔS_M as large as 350 J kg⁻¹ K⁻¹ at 310 K for a field change of 5 T, which is far above any other results reported up to date,⁷ triggering great disputes on the validity of Eq. (1) on the calculation of ΔS_M for FOMPT.^{8,9} On the other hand, Giguère *et al.*² and Balli *et al.*⁹ claimed that the following Clausius–Claperyon (CC) equation:

$$\Delta S_M(T,B) = -\Delta M \frac{dH_c}{dT},\tag{2}$$

is more convincible in the calculation of FOMPT's ΔS_M , instead of Eq. (1). Here, ΔM is the difference of magnetization between low- and high-field phases. H_c is the critical field which induces the metamagnetic phase. But, given that the thermodynamic potential can be an exact differential as well as considering FOMPT as an instantaneous transition, Sun *et al.*⁴ proved the equivalence of Eq. (1) with Eq. (2). This makes the problem even further complicated. If Eq. (1) and Eq. (2) are equivalent in the FOMPT's ΔS_M calculation, why in real calculation, the values by Eq. (1) are sometimes significantly higher than those by CC equation. Therefore, we are motivated to figure out the origin of such overestimation of the so-called "colossal" ΔS_M and the spurious "spike" on $\Delta S_M - T$ curves obtained by direct application of Eq. (1). In this work, we will show that such significant discrepancy is due to the improper application of Eq. (1). By considering the temperature-dependent mass variation in ferromagnetic (FM) and paramagnetic (PM) phases, large discrepancy disappears and the obtained results are consistent well with those obtained by CC equation.

Generally, for a second-order phase transition or a FO-MPT in a single-phase region between temperatures T_1 and T_2 , as shown in Fig. 1(a), the ΔS_M is proportional to the difference of the magnetization work (Σ_1), which numerically equals to the area enclosed between two isothermal magnetization curves [Fig. 1(a)]. Direct application of the Maxwell relation [Eq. (1)] for calculating FOMPT's ΔS_M is valid in this temperature region, based on a fact that the mass of FM phase maintains constant. But this crucial condition is always neglected in the ΔS_M calculation by the Maxwell relation in the two-phase region.

With increasing temperature to the two-phase region [for example, T_3 and T_4 as shown in Figs. 1(b) and 1(c)], the situation becomes complicated. The initial step indicates the saturation of FM phase. At higher field, a magnetization jump indicates a field-induced PM to FM phase transition accompanied with structural transition. Due to the coexistence of FM and PM phases, at temperature *T* without applied field, the ratios [f(T) and p(T)] for FM and PM phases can be estimated as follows:

$$f(T) = \frac{M_f(T)}{M_t(T)}$$
 and $p(T) = 1 - f(T)$. (3)

Here, as seen in Fig. 1(c), M_f is the magnetization contributed only by FM phase in the mixture obtained by extrapolation. M_t is the saturation magnetization at high field when the PM phase is totally transformed into FM phase. If Maxwell relation was directly applied, based on Eq. (1), the ΔS_M would be written as follows:

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FIG. 1. (Color online) Illustration of FOMPT's isothermal magnetization procedure at low temperature T_1 and T_2 (a), two-phase region T_3 (b), and T_4 (c) ($T_1 < T_2 < T_3 < T_4$). Σ_1 stands for the magnetization work subtraction between T_1 and T_2 , which numerically equals to the area enclosed between isothermal magnetization curves at T_1 and T_2 . Σ_2 and Σ_4 stand for the magnetization works of FM phase at T_3 and T_4 , respectively, which numerically equal to their respective corresponding areas. Σ_3 and Σ_5 stand for the PM counterparts at T_3 and T_4 . $f(T_3)$ and $f(T_4)$ stand for the FM ratio at T_3 and T_4 , respectively.

$$\Delta S_M(T, \Delta B) = \frac{(\Sigma_4 + \Sigma_5) - (\Sigma_2 + \Sigma_3)}{T_4 - T_3}.$$
(4)

Here, as shown in Figs. 1(b) and 1(c), Σ_4 and Σ_5 , are the respective magnetization work of the FM and PM phases at T_4 . Σ_2 and Σ_3 are the counterparts at T_3 . However, it should be also noted that magnetization work Σ_4 at T_4 is contributed from the FM phase, which is $f(T_4)$ of total working amount. But magnetization work Σ_2 at T_3 is contributed from FM phase which is $f(T_3)$ of total working amount. It indicates that the magnetization works are contributed from different mass of working materials, which is temperature-dependent. Similar situation would be for PM phase. Direct subtraction between $(\Sigma_4 + \Sigma_5)$ and $(\Sigma_3 + \Sigma_2)$ would contain not only the contribution of moment change due to temperature but also the amount change due to temperature. Such subtraction is meaningless and unreasonable, leading to the "colossal" MCE and the so-called "spike." It is the origin of large discrepancy between the ΔS_M values obtained directly by Maxwell relation [Eq. (4)] and by the CC equation [Eq. (2)].

In order to obtain reasonable ΔS_M by Maxwell relation, before subtracting the magnetization works of different temperature, we have to compare the magnetization works contributed from same amount of FM phases and tick out the unreasonable contribution due to the mass change. For example, at temperature T_4 , the modified Maxwell relation should be as follows:



FIG. 2. (Color online) Temperature dependence of FM phase ratio in $MnAsC_{0.015}$ (a), $MnAsC_{0.03}$ (b), $Mn_{0.985}Al_{0.015}As$ (c), and $Mn_{0.994}Fe_{0.006}As$ (d). These data in (d) are deduced from Fig. 6 in Ref. 7.

$$\Delta S(T_4, \Delta B) = \frac{1}{T_4 - T_3} \left\{ \left[\Sigma_4 - \frac{\Sigma_2}{f(T_3)} f(T_4) \right] + \left[\Sigma_5 - \frac{\Sigma_3}{p(T_3)} p(T_4) \right] \right\},$$
(5)

here $\sum_{2} f(T_{3})$ is the imaginary magnetization work at temperature T_3 if the working material is entirely FM phase. Considering that at T_4 FM phase is only $f(T_4)$ of total working material, $\sum_{2} f(T_{4}) / f(T_{3})$ is the imaginary magnetization work at temperature T_4 . In this way, both Σ_4 and $\sum_{2} f(T_4) / f(T_3)$ could be compared based on the same quantity of FM phase. The item in the first parenthesis is the real magnetization work subtraction only contributed by FM's moment changes without contribution due to the mass changes. The second one is the PM's counterpart. Compared with the original Maxwell relation, the temperaturedependent mass variation in two-phase region is considered in Eq. (5). If the working material is homogenous during phase transition, f(T) would be temperature-independent and Eq. (5) would be same with original Maxwell relation [Eq. (4)].

Since we have demonstrated the origin for the large discrepancy in ΔS_M estimation and indicated the proper way of calculating the MCE by Eq. (5), in the following part, we will demonstrate such calculations with MnAsC_{0.015}, MnAsC_{0.03},¹⁰ Mn_{0.985}Al_{0.015}As,¹¹ and Mn_{0.994}Fe_{0.006}As (Ref. 7) compounds as examples. In order to calculate the ΔS_M , the temperature dependence of the FM ratio in the two-phase region should be first determined, as shown in Fig. 2. The FM ratio decreases with increasing temperature. Based on the temperature dependence of the FM ratio, the temperature dependence of the ΔS_M of MnAsC_{0.015}, MnAsC_{0.03}, and Mn_{0.985}Al_{0.015}As for a field change of 5 T, is calculated by using Eq. (5). Comparisons are shown in Figs. 3(a)–3(c) with those obtained by directly applying the Maxwell relation [Eq. (4)], and by the CC equation [Eq. (2)].

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FIG. 3. (Color online) Temperature dependences of magnetic entropy changes in MnAsC_{0.015} (a), MnAsC_{0.03} (b), Mn_{0.985}Al_{0.015}As (c), and Mn_{0.994}Fe_{0.006}As (d) for the field change of 5 T calculated by Eq. (5). The ΔS_M data of MnAsC_{0.015}, MnAsC_{0.03}, and Mn_{0.985}Al_{0.015}As calculated by direct application of Maxwell relation [Eq. (4)] are referred to Ref. 10 and Fig. 3 of Ref. 11. The ΔS_M data of Mn_{0.994}Fe_{0.006}As calculated by directly application of Maxwell relation [Eq. (4)] and CC equation [Eq. (2)] are referred to Fig. 4 in Ref. 7 and Fig. 3 in Ref. 9.

The dH_C/dT used in the CC equation [Eq. (2)] are determined to be about 0.2 T/K, 0.25 T/K, and 0.25 T/K for MnAsC_{0.015}, MnAsC_{0.03}, and Mn_{0.985}Al_{0.015}As compounds, respectively. It can be seen that the spikes disappear on the $\Delta S_M - T$ curves determined by Eq. (4). The ΔS_M values are almost consistent with those calculated by the CC equation [Eq. (2)], indicating the validity of this modified approach. The real $-\Delta S_{max}$ for MnAsC_{0.015}, MnAsC_{0.03}, and Mn_{0.985}Al_{0.015}As compounds for a field change of 5 T are estimated to be about 9.8 J kg⁻¹ K⁻¹ at 287 K, 14.7 J kg⁻¹ K⁻¹ at 279 K, and 18.1 J kg⁻¹ K⁻¹ at 273 K, respectively.

In order to further confirm the validity of the modified approach, the ΔS_M of Mn_{0.994}Fe_{0.006}As for a field change of 5 T are recalculated by using Eq. (5) and compared with the data given in Refs. 7 and 9, as shown in Fig. 3(d). It can be seen that the discrepancy are more significant than those in Figs. 3(a)-3(c). This is because the FM ratio f(T)decreases more rapidly with increasing temperature [see Fig. 2(d)]. But the ΔS_M obtained by Eq. (5) is well consistent with that obtained by the CC equation [Eq. (2)], confirming that such large discrepancy originates from neglecting the temperature-dependent FM and PM masses variation in the two-phase region. The Maxwell relation can be applied in calculating the FOMPT's ΔS_M , if the mass changes in the FM and PM phases are considered.

In conclusion, we have explained the origin of the large discrepance by direct application of the Maxwell relation and given the proper approach in estimating FOMPT's ΔS_M in two-phase region. By considering the mass changes in the FM and PM phases, the ΔS_M values estimated by the modified Maxwell relation are well consistent with those obtained by the CC equation, confirming the validity of the calculation approach we proposed for FOMPT's ΔS_M and its equivalence with the CC equation in the region of two-phase region.

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