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Overcoming the spin-multiplicity limit of entropy by means of lattice degrees of freedom: a minimalist model

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The discovery of the giant magnetocaloric effect with isothermal field-induced entropy change beyond the spin-multiplicity limit gave rise to some indistinctness in the literature regarding the applicability of fundamental thermodynamics in data analysis. Those misleading interpretations concerning for instance the rigorousness of phenomenological thermodynamics are clarified here. Specifically, it is shown that the Maxwell relation incorporates contributions from the spin degrees of freedom and potential lattice degrees of freedom into the isothermal entropy change. A minimalist model involving pairs of exchange coupled, mobile Ising spins is investigated. It is explicitly shown that lattice degrees of freedom can be activated via applied magnetic fields and the integrated Maxwell relation contains this lattice contribution. A simple and intuitive analytic expression for the isothermal entropy change in the presence of field-activated lattice degrees of freedom is provided.

Introduction

The quest for advanced magnetocaloric materials has intensified in recent years due to their important role in future energy-efficient and environmentally friendly refrigeration technologies.[1,2,3,4,5,6,7,8,9,10]. An appreciable magnetocaloric effect (MCE) with sizeable isothermal entropy change and adiabatic temperature change in moderate applied magnetic fields requires new magnetic materials with tailored magnetocaloric properties. This search defines one of the today's materials science frontiers[11,12,13,14]. Most of the present research activities focus on the giant MCE found in bulk rare earth alloys[15,16,17,18,19,20,21,22]. Recently, even nanotechnological approaches have been exploited to tailor microscopic magnetic parameters such as exchange and anisotropy for advanced magnetocaloric materials design[23,24,25,26,27]. However, recent discoveries of a giant MCE, which permit overcoming the magnetic limit[28,29,30] for the isothermal entropy change, make it evident that optimization of magnetic interactions alone will not suffice for ultimate optimization of the MCE. Sparked by this insight, an even more intensified but perhaps somewhat unfocused search for new giant MCE materials can be observed in recent years.

Despite the growing quantity of publications and growth of insight it seems clear that some fundamental aspects of thermodynamics and statistical mechanics appear to be overlooked by some in the literature, leading to statements such as "… the colossal MCE was obtained from magnetic measurements using Maxwell’s relation, which only reflects changes in magnetic entropy."[31] More commonly, many authors refer to the isothermal entropy change, which is the entropy change at constant temperature, *T*, induced by a change of the magnetic field, as magnetic entropy change[32,33,34,35,36]. This nomenclature can be very misleading and appears to be subliminally interpreted by others, not explicitly referenced here, as a contribution to the entropy change which exclusively originates from spin degrees of freedom. This interpretation is in general wrong and can only be applied in the absence of magnetoelastic interactions. We argue here that the use of ΔS_M should be avoided, the index, M, should be suppressed, and the term isothermal entropy change should be used instead. In contrast to certain statements in the literature it is not a matter of debate whether the integrated Maxwell relation contains all of the field-induced isothermal entropy change for systems in a homogeneous phase. If the Maxwell relation is applicable, meaning the second order mixed derivatives of the Gibbs free energy are mathematically well defined and identical, the isothermal entropy change obtained from integration of the magnetization derivative contains all possible field-induced contributions. Among our goals here is to convey this message following the tradition of manuscripts such as the work by Pecharsky et al. in Ref.(37) discussing fundamental aspects of the underlying thermodynamics of the MCE.

In addition, there seems to be some confusion about the conditions allowing for contributions of lattice degrees of freedom to the isothermal entropy change. The vagueness often seen in discussions on this subject has the potential to confuse materials scientists searching for magnetocaloric materials which overcome the magnetic limit for the isothermal entropy change. The latter is determined by the logarithm of $2J+1$, where J is the total atomic angular moment when a localized moment picture can be applied. One can anticipate that magnetic materials relying only on the limited J-multiplicity for isothermal entropy change will not be able to compete with the proposed electrocaloric materials.[38] Here, quantization is not the limiting factor and large changing electric fields are much easier realized than changing magnetic fields. Therefore, competitive magnetocaloric materials need to make use of entropy contributions of non-magnetic degrees of freedom which still can be activated through magnetic fields.

The objective of this work is twofold. First, we aim to reemphasize the rigorous nature of relations from phenomenological thermodynamics such as the Maxwell relation. Special emphasis is on the fact that the isothermal entropy change determined via Maxwell's relation is not limited to magnetic degrees of freedom. Second, we investigate a model system which we consider to be as simple as possible and as complex as necessary to show under which conditions lattice degrees of freedom can be activated and contribute to the magnetic field-induced isothermal entropy change. We finally bring these two points together and show explicitly that the integrated Maxwell relation contains this lattice contribution, if present, despite the fact that the field integral is taking place over the temperature derivative of the magnetization. It is the absence of elastic variables in the Maxwell relation which, in a naïve view, may appear counterintuitive and, hence, can lead to the wrong conclusion that field-dependent lattice effects are not included in this integral.

Contributions to the isothermal entropy change which are not magnetic in origin can only exist if there is coupling between spin and elastic degrees of freedom giving rise to a free-energy coupling-term with a dependence on the magnetic field, H, such that the total Gibbs free energy, G, reads $G_{total}(T,H) = G_{spin}(T,H) + G_{lattice}(T) + G_{spin-lattice}(T,H)$. It is the field dependent spin-lattice contribution, $G_{spin-lattice}(T,H)$, which creates the possibility of overcoming the multiplicity limit $\Delta S_{\max}^{J} = S_J(H=0) - S_J(H \to \infty) = nR\ln\left(2J+1\right)$. The latter spin-multiplicity limit $\Delta S^{J}{}_{\max}$ originates from $S_J(T,H) := -\left(\partial G_{spin}/\partial T\right)_H$ and has therefore no contribution from the lattice degrees of freedom, because the regular term $G_{lattice}$ has no field dependence. We show explicitly in a minimalist microscopic model that a term of the form $G_{spin-lattice}(T,H)$ contributing to the isothermal entropy change requires non-linear spin-lattice coupling. Evidently, magnetocaloric materials can only take advantage of lattice degrees of freedom if non-linear coupling is sizable. We use our minimalistic Hamilton function to calculate the Gibbs free energy and from that the isothermal entropy change showing the possibility of overcoming $\Delta S_{\max}^{J}$. Moreover, we calculate the magnetization, $M(T,H)$, and show for the latter that in fact the numerically integrated Maxwell relation can generate an isothermal entropy change $\Delta S > nR\ln\left(2J+1\right)$ which of course is identical with the analytically derived ΔS using the free-energy expression. This explicit proof given by our specific model may retrospectively appear redundant because one may argue that there is no need to reconsider established thermodynamics. However, the existing tendency to reason on the basis of models and microscopic considerations together with a general propensity to consider statistical physics superior to phenomenological thermodynamics is motivation enough for the explicit confirmation of the integrated Maxwell relation. The work outlined here serves as an explicit reminder that the Maxwell relation, when the prerequisites for its application are fulfilled, provides the complete isothermal entropy change and not just a "magnetic contribution" in case there is more. We hope that our considerations help to clarify some of the recent confusions such as those about Maxwell's relation in the framework of discussions of the lattice contributions to the isothermal entropy change.

Minimalist Classical Model Hamiltonian

We consider an ensemble of statistically independent constituents of pairs of interacting, mobile classical Ising spins. When neglecting the kinetic energy, the Hamiltonian of an individual Ising spin-pair reads

$$H = \frac{1}{2}D\left(x_2 - x_1\right)^2 + J(x_1, x_2)\sigma_1\sigma_2 - h\left(\sigma_1 + \sigma_2\right). \tag{1}$$

Here, D is the curvature of the harmonic elastic energy, $J(x_1, x_2)$ is the exchange integral, $\sigma_{1,2} = \pm 1$ are the classical Ising spin variables, and h is an applied magnetic field where constants like the Bohr magneton, the g-factor and the vacuum permeability have been absorbed such that h is measured in units of energy. Eq.(1) is a minimalistic version of the 1-dimensional Ising model with mobile spins similar to the one discussed in the appendix of Ref.(39). We allow for an additional Zeeman term and enable non-linear spin-lattice interaction via the general dependence of the exchange integral on $x_{1,2}$ quantifying the deviations from the equilibrium positions of the atoms 1 and 2. We make the assumption of an exponential dependence of the exchange integral on the spatial separation of the two spins which reads[40]

$$J\left(x_1, x_2\right) = J_0\, e^{-(x_2 - x_1)/a}, \tag{2}$$

where a determines the length scale on which the exchange interaction decays. We restrict our consideration to the case of small deviations from the equilibrium positions such that $\left(x_2 - x_1\right)/a$ becomes a small parameter. We use the latter to expand Eq.(2) up to first order and second order, respectively. Substituting this expansions into Eq.(1) leaves us with two systematically progressing approximations H_α and H_β of our minimalistic model Hamiltonian

$$\begin{aligned} H_\alpha &= \frac{1}{2}Dy^2 + J_0\left[1 - \frac{y}{a}\right]\sigma_1\sigma_2 - h\left(\sigma_1 + \sigma_2\right) \\ H_\beta &= \frac{1}{2}Dy^2 + J_0\left[1 - \frac{y}{a} + \frac{y^2}{2a^2}\right]\sigma_1\sigma_2 - h\left(\sigma_1 + \sigma_2\right) \end{aligned}, \tag{3}$$

where $y = x_2 - x_1$ is proportional to the normal coordinate of the vibrational motion.

Next we evaluate the canonical partition function and from that the Gibbs free energy per spin pair for H_α and H_β, respectively. We integrate out the classical variable $0 \le y/a \le \infty$ and take into account the spin products $\{\sigma_1\sigma_2\}=\{1,-1,-1,1\}$ and spin sums $\{\sigma_1+\sigma_2\}=\{2,0,0,-2\}$ of the 4 spin configurations. As a result we obtain for H_α in the limit of small exchange energy in comparison with the elastic and the thermal energy k_BT. This limit justifies neglecting quantum considerations including the kinetic energy term in the Hamiltonian and leads to

$$G_\alpha(T,h)=(2h+J_0)-\frac{J_0^{\,2}}{2a^2D}-k_BT\ln\left(1+e^{\frac{4h}{k_BT}}+2e^{\frac{2(h+J_0)}{k_BT}}\right)-k_BT\ln\sqrt{\frac{\pi k_BT}{2a^2D}}\,. \tag{4}$$

We are interested in the isothermal entropy change $\Delta S=S(T,h=0)-S(T,h\to\infty)$. Therefore, only the term $\tilde{G}_\alpha=-k_BT\ln\left(1+e^{\frac{4h}{k_BT}}+2e^{\frac{2(h+J_0)}{k_BT}}\right)$ of Eq. (4) which depends on h and T needs to be considered. It is straightforward to show from the temperature derivative of $\tilde{G}_\alpha$ and intuitively that asymptotically for $k_BT \gg |J_0|$ the maximum isothermal entropy change becomes ΔS_α $=S_\alpha(T,h=0)-S_\alpha(T,h\to\infty)=k_B\ln 4$. This is in accordance with $\Delta S_{\max}=2k_B\ln 2$ obtained from the limiting expression given by the logarithm of the spin-multiplicity of a quantum mechanical spin 1/2 system where 2 such spins are involved in our model Hamiltonian. Evidently, the spin-lattice coupling in linear approximation has no effect on the isothermal entropy change induced by a magnetic field in the classical limit. In fact the term $\tilde{G}_\alpha$, which completely determines the isothermal entropy change, does not depend on the parameter a which controls the spin-lattice coupling. A model Hamiltonian of the form H_α is therefore not able to create an entropy contribution which originates from non-magnetic degrees of freedom.

The situation changes when considering H_β. Again we restrict ourselves to the limiting case where the elastic energy is large in comparison to the exchange energy and temperatures are sufficiently high. Then the Gibbs free energy G_β reads

$$G_\beta(T,h)=\left(2h+J_0\right)-k_BT\ \ln\left(e^{-\frac{J_0(4h+3J_0)-4a^2D(h+J_0)}{2\left(a^2D-J_0\right)k_BT}}\sqrt{\frac{2\pi k_BT}{a^2D-J_0}}+\sqrt{\frac{\pi k_BT}{2\left(a^2D+J_0\right)}}\left(e^{\frac{4h}{k_BT}+\frac{J_0^2}{2k_BT\left(a^2D+J_0\right)}}+e^{\frac{J_0^2}{2k_BT\left(a^2D+J_0\right)}}\right)\right).\text{(5)}$$

It is straightforward to show that in the limit of large *a* Eq.(5) reduces to Eq.(4) up to an irrelevant field and temperature independent constant. In contrast to Eq.(4) we see that the non-linear Hamiltonian H_β generates terms in the free energy, which depend on the magnetic field, temperature, and exchange as well as the elastic constant *D*. Next we show that this is the ingredient allowing for $\Delta S > k_B \ln\left(2J+1\right)$ via a magnetic field-activation of non-magnetic degrees of freedom through non-linear spin-lattice coupling.

From $S=-\left(\partial G_\beta/\partial T\right)_h$ we calculate $\Delta S_\beta(T,h)=S_\beta\left(T,h=0\right)-S_\beta\left(T,h\right)$ in the limit $k_BT>>\left|J_0\right|$ which simplifies in the limit $\Delta S_\beta\left(T,h\to\infty\right)=S_\beta\left(T,h=0\right)-S_\beta\left(T,h\to\infty\right)$ into the intuitive approximate expression

$$\Delta S_\beta\left(T,h\to\infty\right)=\frac{k_BJ_0}{2a^2D}+k_B\ln 4 \tag{6}$$

showing that the conventional limit determined by the logarithm of the spin-multiplicity is exceeded by the term $\frac{k_BJ_0}{2a^2D}$ which allows for an intuitive interpretation.

Clearly, in the absence of spin-spin exchange such as paramagnetic materials, entropy originating from elastic degrees of freedom cannot be harnessed. Likewise, a sensitive dependence of the exchange on the spatial spin separation expressed in accordance with Eq.(2) through a small characteristic exponential decay length *a* increases spin-lattice coupling and enhances the impact of the lattice degree of freedom on the entropy change. Finally, if the elastic energy a^2D is large in comparison with k_BT, there is no significant thermal excitation of the elastic degree of freedom and, hence, no significant contribution from the latter to the isothermal entropy change.

Comparison between integrated Maxwell relation and entropy of the model Hamiltonian

Next we calculate the magnetization $M = -\left(\partial G_\beta(T,h)/\partial h\right)_T$ and use the resulting M vs. h isotherms for numerical integration of the Maxwell relation, $\left(\frac{\partial M}{\partial T}\right)_h = \left(\frac{\partial S}{\partial h}\right)_T$. The latter provides the isothermal entropy change ΔS as a function of h. The result from the Maxwell relation is then compared with the analytically calculated isothermal entropy change determined directly from $S = -\left(\partial G_\beta/\partial T\right)_h$. This comparison provides explicit confirmation that the Maxwell relation includes the lattice degrees of freedom.

Specifically, we calculate the magnetic moment per spin pair for the set of parameters a=0.7, $J_o = 0.1$ and D=1. These values fulfill the constraint $a^2 D >> J_o$ under which we performed the classical calculation of the Gibbs free energy based on the Hamiltonian H_β. In addition we limit our investigation to a temperature region such that $k_B T$ is large in comparison with elastic and exchange energies such that our classical consideration becomes meaningful.

Figure 1 shows a representative set of isotherms M vs. h for $4 \leq T \leq 100$ in temperature steps of $\Delta T = 2$. The complete data set used for the entropy calculation via Maxwell's relation involves the isotherms for $3 \leq T \leq 100$ in steps of $\Delta T = 0.01$.

Figure 2 shows the entropy calculated via the integrated Maxwell relation (magenta open circles) using the magnetization data selectively displayed in Figure 1. The black solid lines in Figure 2 show the isothermal entropy change $\Delta S_\beta(T,h)$ calculated analytically from

$S = -\left(\partial G_\beta / \partial T\right)_h$. For clarity $\Delta S_\beta(T,h)$ curves are displayed in field step of $\Delta h = 2$. The perfect coincidence of circles with the lines implies that the Maxwell relation contains the entropy contributions of both the spin degrees of freedom as well as the lattice degrees of freedom. There is, within numerical uncertainties, no difference between the result from the integrated Maxwell relation and $\Delta S_\beta(T,h)$ calculated analytically from $S = -\left(\partial G_\beta / \partial T\right)_h$.

The lower dotted blue line in Figure 2 represents the value of $\Delta S^J_{\max}$ which for $J = 1/2$ reads $\Delta S^J_{\max} / k_B = 2\ln 2 = 1.38$. The upper dotted red line shows the maximum isothermal entropy change achievable in our model with magnetoelastic coupling using the microscopic parameters above. This limit is clearly above the magnetic limit $\Delta S^J_{\max} / k_B = 2\ln 2$ indicating explicitly that lattice degrees of freedom can contribute to the isothermal field-induced entropy change as they do in real systems in the case of the giant MCE. The validity of our simple approximate Eq.(6) is also prominently evident in this figure. A calculation of the limiting approximate expression $\Delta S_\beta\left(T,h \to \infty\right) = \dfrac{k_B J_0}{2a^2 D} + k_B \ln 4$ yields $\Delta S_\beta\left(T,h \to \infty\right) = 1.488 k_B$ which is in excellent agreement with our numerically calculated value of $\Delta S_\beta\left(T,h \to \infty\right) = 1.494 k_B$.

The inset of Fig. 2 shows a semi-logarithmic plot of $Area(T) = -\dfrac{1}{k_B}\int_0^T \Delta S(T')\, dT'$ evaluated through numerical integrations of the $-\Delta S / k_B$ vs. T data for h=30. An area sum rule is known to hold such that $\lim_{T\to\infty} Area(T) = \mu_0 V M_s \Delta H / k_B$ where VM_s is the saturation magnetic moment and ΔH is the magnetic field change which induces the isothermal entropy change.[29] In accordance with the area sum rule, our numerically calculated function *Area*(T) shows an asymptotic approach of the limiting value $\mu_0 V M_s \Delta H$ which is given by the saturation value $\left(\sigma_1 + \sigma_2\right) h = 60$

in the reduced variables of our model with h=30 and $\sigma_{1,2}$=1. The fact that the sum rule applies is further evidence that the Maxwell relation includes all contributions to the entropy change, including those originating from elastic degrees of freedom.

Summary

We have clarified the misleading interpretation of what is sometimes called in the literature magnetic entropy change. The magnetic field-induced isothermal entropy change can in fact contain lattice contributions other than just spin degrees of freedom. In addition we reemphasized that those contributions are fully contained in the Maxwell relation if the latter is applicable. We used a minimalistic model of Ising spin pairs and made it as complex as necessary to show that the activation of lattice degrees of freedom requires non-linear magnetoelastic coupling. Moreover, we showed explicitly that lattice degrees of freedom can help to overcome the spin-multiplicity limit of entropy as it does in the giant magnetocaloric effect. Here, however, we show the impact of elastic coupling on the magnetocaloric effect already in the absence of magnetic long range order.

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Figure captions

Fig. 1: Representative isotherms M vs. h for $0 \leq h \leq 30$ calculated with a=0.7, $J_o = 0.1$ and D=1 for $4 \leq T \leq 100$ displayed in steps $\Delta T = 2$.

Fig. 2.(color online): Entropy $\Delta S_{\beta}(T,h)$ (black solid lines) versus T calculated from Gibbs free energy derivatives for a=0.7, $J_o = 0.1$ and D=1 displayed at constant magnetic fields $2 \leq h \leq 30$ in field steps $\Delta h = 2$. Open circles (magenta) show entropy calculated via Maxwell relation using magnetization data such as the isotherms shown in Fig.1. The lower dotted blue line represents the maximum entropy limit based of spin-multiplicity only. The upper dotted red line shows the maximum isothermal entropy change which includes the magnetoelastic contribution using the microscopic parameters a=0.7, $J_o = 0.1$ and D=1. The inset shows the result of the temperature dependent area determined from numerical integration of the -ΔS vs T curve for h=30. The dashed horizontal line marks its theoretical limiting value of 60.

References

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[1]V. K. Pecharsky, K. A. Gschneidner Jr., Int. J. Refrigeration **29,** 1239 (2006).

[2] V. K. Pecharsky, K. A. Gschneidner Jr., J. Magn. Magn. Mat. **200**, 44 (1999).

[3] S.L. Russek, C. Zimm, Int. J. Refrigeration **29**, 1366 (2006).

[4] K.A. Gschneidner Jr., V.K. Pecharsky, A.O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).

[5]V. K. Pecharsky, K. A. Gschneidner Jr., Int. J. Refrigeration **29,** 1239 (2006).

[6] V. K. Pecharsky, K. A. Gschneidner Jr., J. Magn. Magn. Mat. **200**, 44 (1999).

[7] S.L. Russek, C. Zimm, Int. J. Refrigeration **29**, 1366 (2006).

[8] K.A. Gschneidner Jr., V.K. Pecharsky, A.O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).

[9] C. Zimm, A. Boeder, J. Chell, A. Sternberg, A. Fujita, S. Fujieda, K. Fukamichi, Int. J. Refrigeration **29**, 1302 (2006).

[10] http://en.wikipedia.org/wiki/Magnetocaloric_effect and references there in.

[11] V. Provenzano, A. J. Shapiro and R. D. Shull, Nature **429,** 853 (2004).

[12] T. Krenke, E. Duman, M. Acet, E.F. Wassermann, X. Moya, L. Manosa, and A. Planes, Nature Mat. **4**, 450 (2005)

[13] O. Tegus, E. Brueck, K. H. J. Buschow, and F. R. de Boer, Nature **415**, 150 (2002).

[14] V. K. Pecharsky, A. P. Holm, K. A. Gschneidner, Jr., and R. Rink, Phys. Rev. Lett. **91**, 197204 (2003).

[15] C.S. Aleves, S. Gama, A. de A. Coelho, E. J. R. Plaza, A. M. G. Carvalho, L. P. Cardoso, and A. C. Persiano, Materials Research **7**, 535-538 (2004).

[16] Campos A, Rocco D L, Magnus A, Carvalho G, Caron L, Coelho A A, Gama S, Silva L M D, Gandra F C G, Santos A O D, Cardoso L P, von Ranke P J and de Oliveira N A, Nature Materials, **5**, 802-804 (2006).

[17] S. Fujieda, A. Fujita, and K. Fukamichi, Appl. Phys. Lett. **81**, 1276 (2002).

[18] S.B. Roy, P. Chaddah, V.K. Pecharsky and K.A. Gschneidner Jr., Acta Materialia **56**, 5895 (2008).

[19] A Giguere *et al*, *J. Phys.: Condens. Matter* **11** 6969 (1999).

[20] T. Samanta, I. Das, and S. Banerjee, Appl. Phys. Lett. **91**, 082511 (2007).

[21] P. Chen, and Y. W. Du, J. Phys. Soc. Jap. **70**, 1080 (2001).

[22] N. K. Sun, S. Ma, Q. Zhang, J. Du, and Z. D. Zhang, Appl. Phys. Lett. **91**, 112503 (2007).

---

[23] T. Mukherjee, S. Sahoo, R. Skomski, D. J. Sellmyer, and Ch. Binek, Phys. Rev. B **79,** 144406 (2009).

[24] R. Skomski, Ch. Binek, S. Michalski, T. Mukherjee, A. Enders, and D. J. Sellmyer, J. Appl. Phys. **107**, 09A922 (2010)

[25] R. Skomski, Ch. Binek, T. Mukherjee, S. Sahoo, and D. J. Sellmyer, J. Appl. Phys. **103**, 07B329 (2008)

[26] S. Thota, Q. Zhang, F. Guillou, U. Lu□ders, N. Barrier, W. Prellier, A. Wahl, P. Padhan, Applied Physics Letters **97**, 112506 (2010)

[27] S. Michalski, R. Skomski, T. Mukherjee, X.-Zh. Li, Ch. Binek, and D. J. Sellmyer, J. Appl. Phys. (accepted).

[28] J. Lyubina, O. Gutfleisch, M. D. Kuz'min, and M. Richter**,** J. Magn. Magn. Mat., **321**, 3571, (2009).

[29] S. Gama, A.A. Coelho, A. de Campos, A.M.G. Carvalho, F.C.G. Gandra, P.J. von Ranke and N.I. de Oliveira, *Phys. Rev. Lett.* **93**, 237202 (2004).

[30] J. D. Zou, H. Wada, B. G. Shen, J. R. Sun and W. Li, EPL, **81**, 47002 (2008)

[31] E.J.R. Plaza, J.C.P.Campoy, J. Magn. Magn. Mat., **321**, 446 (2009).

[32] S Esakki Muthu, N V Rama Rao, M Manivel Raja, D M Raj Kumar, D Mohan Radheep, and S Arumugam, J. Phys. D: Appl. Phys. **43**, 425002 (2010)

[33] S. K. Barik and R. Mahendiran, J. Appl. Phys. **107**, 093906 (2010).

[34] J. Chen, B. G. Shen, Q. Y. Dong, F. X. Hu, and J. R. Sun, Appl. Phys. Lett. **96**, 152501 (2010).

[35] F. X. Hu, J. Wang, L. Chen, J. L. Zhao, J. R. Sun, and B. G. Shen, Appl. Phys. Lett. **95**, 112503 (2009).

---

[36] P. A. Bhobe, K. R. Priolkar, and A. K. Nigam, Appl. Phys. Lett. **91**, 242503 (2007).

[37] V. K. Pecharsky, K. A. Gschneidner, Jr., A. O. Pecharsky, and A. M. Tishin, Phys. Rev. B. 64, 144406 (2001).

[38] A. S. Mischenko , Q. Zhang, J. F. Scott, R. W. Whatmore, and N. D. Mathur, Science **311**, 5765 (2006).

[39] D.C. Mattis and T.D. Schultz, Phys. Rev. **129**, 175 (1962).

[40] Ch. Binek, W. Kleemann, J. Phys. Condens. Matter **4,** 65 (1992).

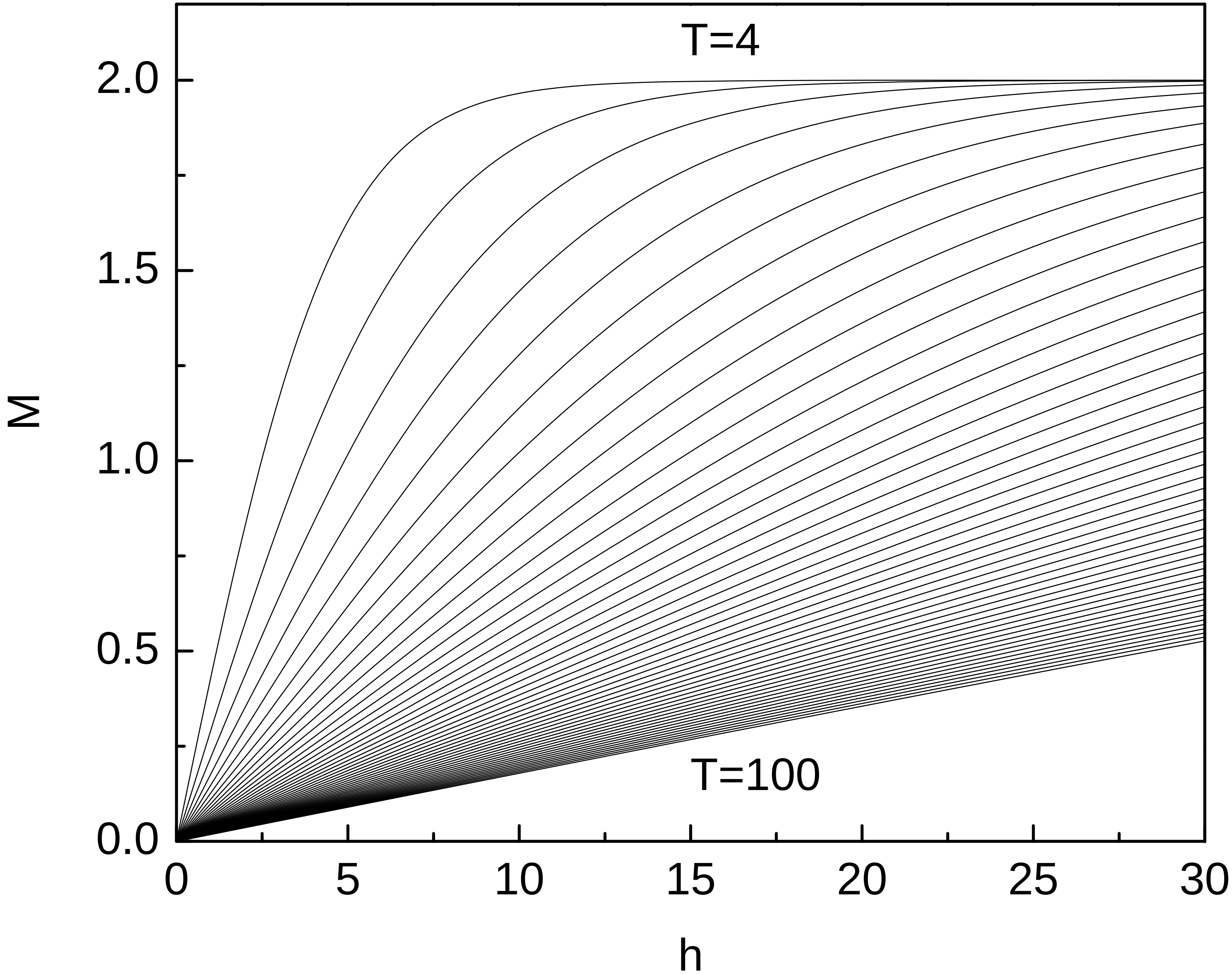
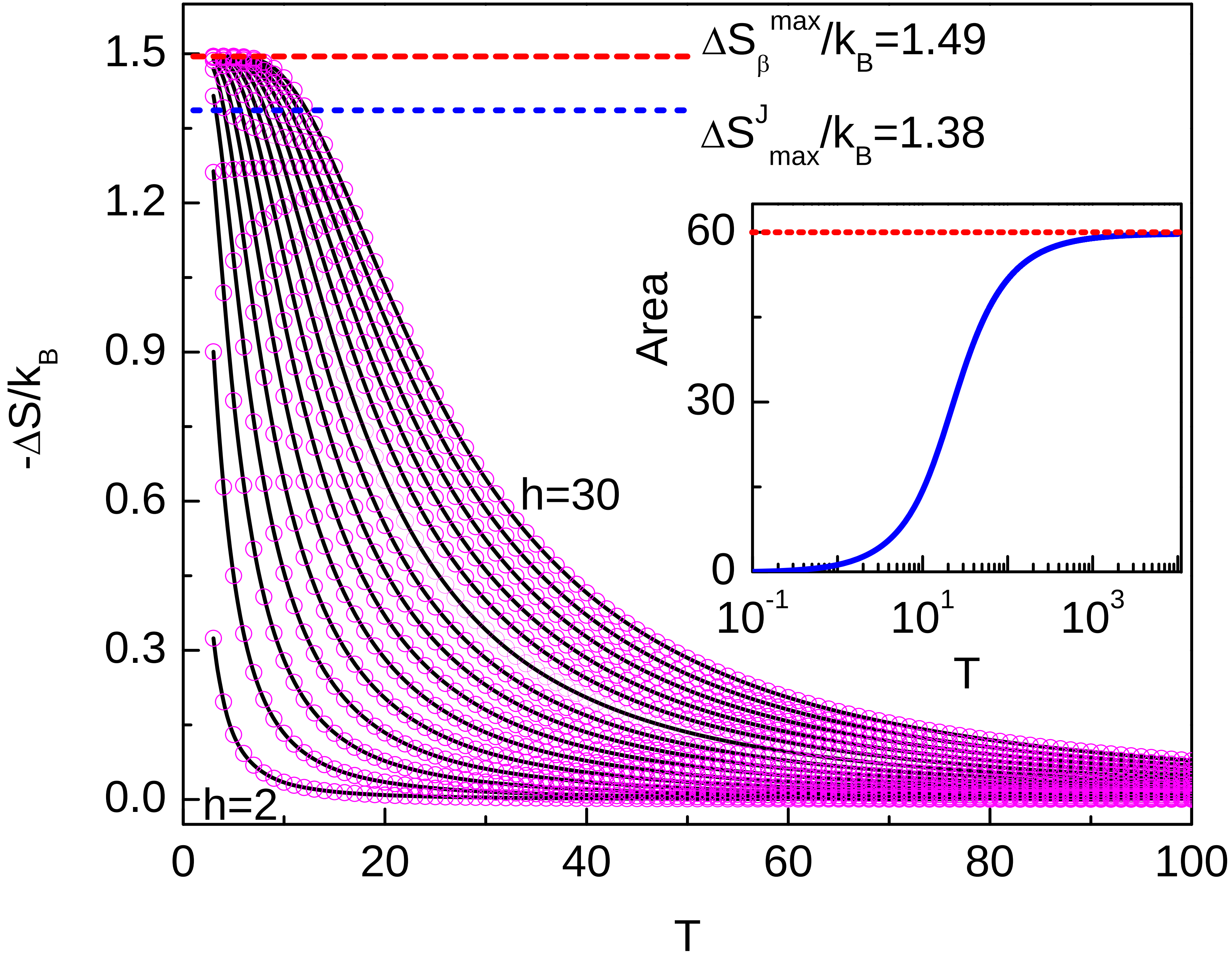


Fig.1



$\Delta S_\beta^{max}/k_B=1.49$
$\Delta S^J_{max}/k_B=1.38$
-ΔS/k_B
1.5
1.2
0.9
0.6
0.3
0.0
h=30
h=2
0
20
40
60
80
100
T
Area
60
30
0
10^{-1}
10^{1}
10^{3}
T

Fig. 2