Physica B 536 (2018) 397–400

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

# Role of entropy in the ground state formation of frustrated systems

Julian G. Sereni

*Low Temperature Div., CAB-CNEA/ANSES, 8400 S.C. de Bariloche, Argentina*

ARTICLE INFO

*Keywords:*
Entropy
Frustrated systems
Nernst postulate

ABSTRACT

The absence of magnetic order in Rare Earth-based frustrated compounds allows to recognize the action of the third law of thermodynamics in the low temperature behavior of those systems. One of the most relevant findings is the appearance of a coincident specific heat $C_m/T|_{T\to 0} \approx 7$ J/molK$^2$ 'plateau' in six Yb systems. This characteristic feature occurs after a systematic modification of the thermal trajectory of their entropies $S_m(T)$ in the range of a few hundred milikelvin degrees. Such behavior is explained by the formation of an *entropy-bottleneck* imposed by the third law constraint ($S_m|_{T\to 0} \geq 0$), that drives the system into alternative ground states. Based in these finding, three possible approaches to the $S_m|_{T\to 0}$ limit observed in real systems are analyzed in terms of the $\partial^2 S_m/\partial T^2$ dependencies.

## 1. Introduction

In the study of the physical properties of new compounds at very low temperature, a number of cases are found not showing magnetic order down to the milikelvin range due to their magnetically frustrated character. All of them exhibit very large density of magnetic excitations ($\propto C_m(T)/T$), which increase at low temperature due to the enhanced spin-correlations in their paramagnetic (Par) state. The observed values of $C_m/T|_{T\to 0}$ exceed those of the classical heavy fermions (HF) because they range between ≈5 [1] and ≈12 J/molK$^2$ [2], allowing to be identified as Very heavy fermions (VHF). These values can be compared with the 3 J/molK$^2$ of the well known non-Fermi-liquid (NFL) $CeCu_{5.9}Au_{0.1}$ [3], at ≈100 mK, which is tuned to a quantum critical point (QCP). Such increase in the density of magnetic excitations, observed in the 'plateau' region of the VHF, is reached following a power law thermal increase ($\propto 1/T^Q$, with $1 \leq Q \leq 1.4$) as shown in Fig. 1. Such a dependence characterizes a quasi-paramagnetic (Par) region where strong spin correlations develop without reaching any ordered configuration.

Six representative examples are included in Fig. 1, showing a common 'plateau' that appears below a characteristic temperature $T^*$. Notably the $C_m/T|_{T\to 0}$ values of all these systems nearly coincide among them at $7 \pm 0.8$ J/molK$^2$, for $PrInAg_2$ [4], YbBiPt [5] and $YbCu_{5-x}Au_x$ [6] with $0.4 \leq x \leq 0.7$. Another compound, $YbCo_2Zn_{20}$ with similar $C_m/T|_{T\to 0}$ values [7], escapes from a simple $C_m(T)/T \propto 1/T^Q$ dependence because of the proximity of its first excited crystal electric field (CEF) doublet which starts to contribute at very low temperature. Notice that no Ce-based compound belongs to this family, including $CeNi_9Ge_4$ [1] with the highest $C_m/T|_{T\to 0} \approx 5$ J/molK$^2$.

The study of VHF systems is becoming relevant because they include some of the new materials recently proposed for the sub-kelvin adiabatic demagnetization refrigeration like $YbPt_2Sn$ [8] and $YbCo_2Zn_{20}$ [9]. In these compounds the application of external magnetic field drastically condenses the high density of excitations producing a huge magneto-caloric effect.

## 2. Discussion

### 2.1. Entropy bottlenecks at the origin of the $T^*$ temperature

The absence of magnetic order down to the milikelvin range in these VHF is verified by different type of measurements. From electrical resistivity ($\rho$) in $YbCu_{5-x}Au_x$ [10] and $PrInAg_2$ [4], the change of regime occurring at $T = T^*$ does not seem to be associated to any magnetic phase transition because $\rho(T)$ decreases continuously around $T^*$, i.e. without any discontinuity in its thermal slope and even revealing the formation of an incipient coherence. The lack of magnetic order in $YbCu_{5-x}Au_x$ down to 0.02 K is confirmed through NQR and $\mu$SR measurements [11]. In order to explore the origin of such behavior one may analyze the trajectory of the thermal parameters like $C_m(T)/T$ and $S_m(T)$ around $T^*$. For such a purpose the well known spin-ice compound $Dy_2Ti_2O_7$ is chosen because its magnetically frustrated character guarantees the absence of magnetic order [13]. Furthermore, this compound shows a more evident change of regime at $T^*$ because $C_m(T)/T$ even decreases for $T < T^*$, see Fig. 2a. In that figure, the fit of the measured $C_m(T)/T$ dependence on the paramagnetic region (i. e. above $T^*$) is included as a continuous curve $C_{Par}/T = 4.6/(T^2 + 0.35)$ [14] that follows a power law thermal dependence.

E-mail address: jsereni@cab.cnea.gov.ar.

http://dx.doi.org/10.1016/j.physb.2017.08.041
Received 1 June 2017; Received in revised form 11 August 2017; Accepted 17 August 2017
Available online 18 August 2017
0921-4526/ 

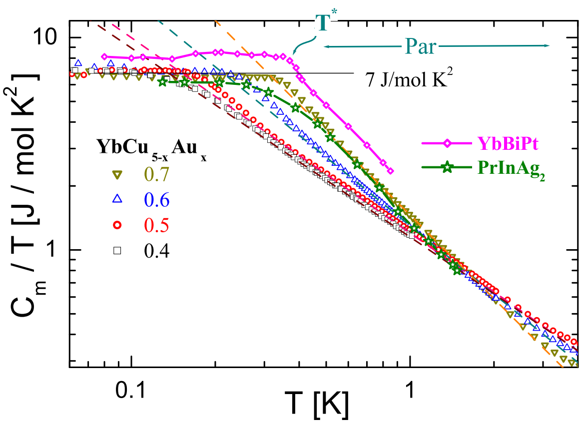


**Fig. 1.** Power law thermal dependence of five VHF in a double logarithmic representation. The 'Par' region identifies the quasi-paramagnetic phase and $T^*$ the temperature of the onset of the $C_m(T)/T$ 'plateau' regime. See the text for references.

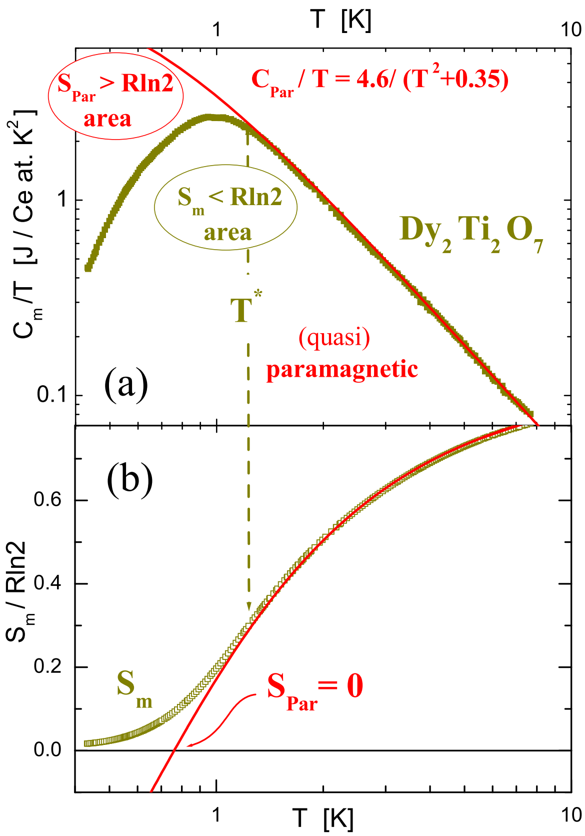


**Fig. 2.** (a) Comparison of thermal dependencies between fitted $C_{Par}(T > T^*)/T$ (red line) and measured $C_m(T)/T$ for the frustrated spin-ice compound $Dy_2Ti_2O_7$ [12]. Notice the double logarithmic representation. $S_{Par}$ and $S_m$ represent the areas for respective entropies evaluation. (b) Thermal dependencies of respective entropies, showing how $S_{Par}(T)$ (continuous curve) crosses $S_{Par} = 0$ at finite temperature.

Also in Fig. 2a, the label $S_{Par}$ identifies the area (entropy $S_{Par}$) computed according to $S_{Par} = \int C_{Par}/T \times dT$ for an ideal system which does not change its $C_{Par}(T)/T$ dependence below $T^*$. Although the computed $C_{Par}(T)/T$ function does not diverge for $T \to 0$, its associated entropy $S_{Par}$ exceeds the 'R ln 2' value corresponding to the doublet ground state (GS) of this compound. As expected, this limit is clearly obeyed by the entropy evaluated from measured $C_m(T)/T$ as $S_m = \int C_m/T \times dT$ that is represented in Fig. 2a by the $S_m$-area. This comparison reveals that the real system undergoes a change of regime at $T = T^*$ compelled by the third law of thermodynamics which states that $S_m|_{T\to 0} \geq 0$.

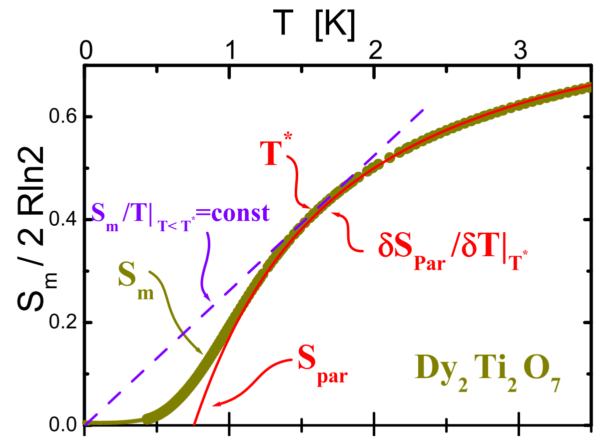


**Fig. 3.** Analysis of the thermodynamic condition producing the entropy deviation from the paramagnetic trajectory. Continuous curve: $S_{Par}(T)$, dashed line: $S_m/T =$ constant.

This analysis is alternatively represented in Fig. 2b through a direct comparison of respective $S_m(T)$ and $S_{Par}(T)$ dependencies. While $S_m(T \leq 1.5\,K)$ deviates from the $T > T^*$ trajectory and points toward the physical limit $S_m|_{T\to 0} = 0$, $S_{Par}(T)$ extrapolates to zero at finite temperature ($T \approx 0.75$ K in this case) and keeps decreasing into unphysical negative ($S_{Par} < 0$) values. Since the change of trajectory in the actual $S_m(T)$ dependence is not induced by magnetic interactions, but driven by the constraint imposed by the third law of thermodynamics ($S_m|_{T\to 0} \geq 0$), $T^*$ can be identified as the temperature at which an *entropy-bottleneck* occurs [15].

Knowing the nature of the changes occurring at $T^*$, the arising question is how to established at which the temperature such *entropy-bottleneck* occurs. Analyzing in Fig. 3 the point at which $S_m(T)$ and $S_{Par}(T)$ split in $Dy_2Ti_2O_7$, one observes that at $T^*$ the $S_m(T < T^*)/T$ ratio and the $\partial S_m/\partial T$ derivative coincide. Since $\partial S_m/\partial T \equiv C_m/T$, it means that $S_m/T|T^* = C_m/T|_{T^*}$ and consequently $S_m = C_m$. Interestingly, the $S_m(T < T^*)/T = \partial S_m/\partial T$ equality implies that $\partial T/T = \partial S_m/S_m$, indicating that at $T = T^*$ the relative variation of the thermal energy ($k_B T$) is the same than the entropy change, i.e. $\partial \ln S_m/\partial \ln T = 1$, as a sort of Grueneisen ratio.

It is illustrative to compare the $S_m(T)$ trajectory analyzed in Fig. 3 with the standard behavior from a magnetically ordered compound. While in the case of a frustrated system the $S_{Par}|_{T<T^*}$ trajectory is always lower than that of the measured one (i.e.$S_{Par}|_{T<T^*} < S_m|_{T<T^*}$), the contrary occurs in the case of a magnetic phase transition because $S_{Par}|_{T<T_{C,N}} > S_m|_{T<T_{C,N}}$, where $T_{C,N}$ indicates Curie or Neel temperatures. These behaviors confirm the physical difference between a thermodynamically driven change of regime and a magnetic transition where the magnetic degrees of freedom are condensed into a singlet GS below $T_{C,N}$, independently of its ordered magnetic structure.

### 2.2. Applicability of the $C_m = S_m$ equality in different systems

In order to recognize the scope of the $C_m = S_m$ equality, one may apply this relationship to different types of not-ordered systems. In Fig. 4 we compare three exemplary cases: a) the previously analyzed 3D frustrated $Dy_2Ti_2O_7$ spin-ice and a 2D frustrated $Ce_2(Pd_{0.5}Ag_{0.5})_2In$. b) One member of the 'plateau' group included in Fig. 1: $YbCu_{4.5}Au_{0.5}$ [6], and c) a NFL representative with one of the highest $C_m/T$ measured values: $CeNi_{8.95}Co_{0.05}Ge_4$ [16].

The former case corresponds to a 3D-frustrated compound where $C_m(T)$ and $S_m(T)$ parameters cross each other at $T^* \approx 1.7$ K. However, taking into account that this spin-ice compound has a residual entropy $S_0 \approx 1.7$ J/mol-at. K [17], by adding this contribution to the measured one as $S_{tot} = S_0 + S_m$ the crossing temperature shifts down to $T^* \approx 1.1$ K, see in Fig. 4a, becoming a sort of tangent-point within the experimental dispersion of the measured data. There are two supports for the use of $S_{tot}$ rather than $S_m$ in the analysis of the discussed

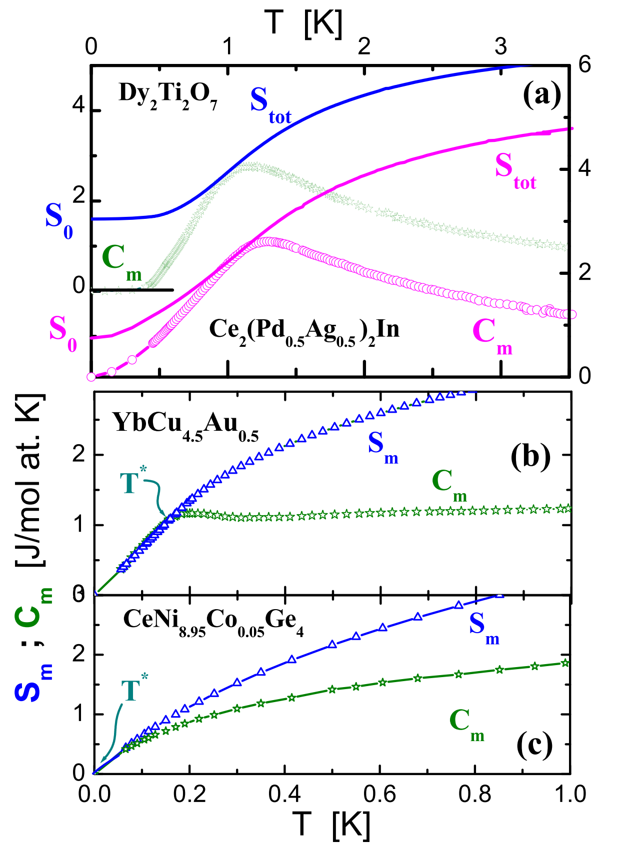


**Fig. 4.** Comparison of $S_m(T)$ and $C_m(T)$ dependencies for three different types of GS: (a) one 3D (left axis) and a 2D (right axis) frustrated compounds. Continuous curves: total entropy $S_{tot} = S_0 + S_{meas}$, including residual ($S_0$) and magnetic ($S_m$) contributions. (b) A member of the 'plateau' type behavior presented in Fig. 1. (c) An exemplary case of NFL behavior [16].

equality. One is because only $S_{tot}$ involves the total expected entropy 'R ln 2' of the doublet GS of this compound. The second arises from the fact that the $S_{tot} - C_m$ difference does not change the sign and is zero where the equality occurs. The same situation occurs with the 2D-frustrated system $Ce_2Pd_{2-x}Ag_x$ In [18] which reaches 84% of the ground state entropy at T≈12 K. Once the 16% of residual entropy is included in $S_{tot}$, the crossing point also becomes a tangent- point at $T^*$.

The case of the 'plateau' group, presented in Fig. 4b, shows that $C_m(T) = S_m(T)$ along $T^* > T > 0$, where $C_m/T|_{T<T^*} = const$. Since in this range of temperature $C_m = \partial H_m/\partial T = H_m/T$ (being $H_m$ the enthalpy), one may write $\Psi = S_m - H_m/T = 0$, being $\Psi$ is the Max Planck potential [19]. The fact that all the systems identified as belonging to the 'plateau' family reach a zero value of a thermodynamic potential for $T < T^*$ may explain their common characteristics.

The latter case ($CeNi_{8.95}Co_{0.05}Ge_4$ in Fig. 4c) is identified as a NFL because of its $C_m \propto -T \times \ln(T/T_0)$ dependence. As it can be seen in the figure, $C_m(T)$ and $S_m(T)$ converge at $T^* = 0$. Interestingly, in this class of materials the difference between $S_m(T)$ and $C_m(T)$ is proportional to the temperature because of their logarithmic dependencies, which also implies that the entropy extrapolates to zero at $T = 0$ despite of the logarithmic divergence of $C_m/T \propto -\ln(T/T_0)$. It is remarkable that in this selected system the stoichiometric compound $CeNi_9Ge_4$, $C_m/T|_{T\to 0}$ tends to a constant value of ≈5 J/molK² [1], whereas less than 1% of Co doping in the Ni lattice changes that behavior into a logarithmic thermal dependence that is typical for systems tuned at a QCP. In fact, for further increase of Co concentration (i. e. ≈3% [16]) an antiferromagnetic phase arises. Similar effect of doping is observed in $Yb_{0.81}Sc_{0.19}Co_2Zn_{20}$ [9] which, like $CeNi_9Ge_4$, exhibits a remarkable low energy first excited CEF levels. In both cases local distortion of the CEF may enhance the effect of disorder destroying the mentioned

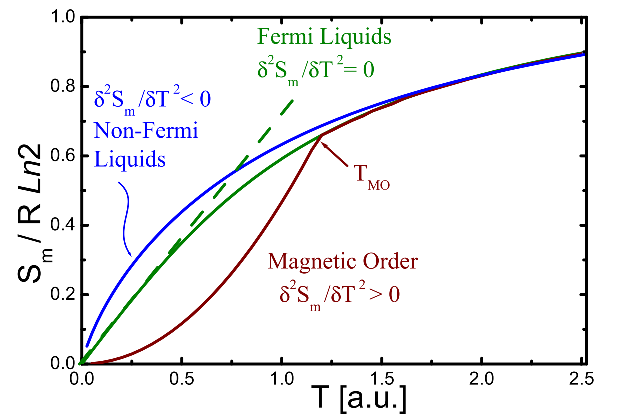


**Fig. 5.** Different ways for $S_m|_{T\to 0}$ according to its second derivative $\partial^2 S_m/\partial T^2$. $T_{MO}$ indicates the magnetic order temperature.

coherence observed in VHF showing a power law dependence of their $C_m(T)/T$ above $T^*$.

### *2.3. Analysis of the thermal dependencies of the entropy at $T \to 0$ in real systems*

Another consequence of the study of magnetic systems which do not reach magnetic order down to the sub-kelvin range is that they provide robust phenomenological information about the actual behavior of the entropy approaching the zero temperature limit. This aspect becomes relevant in the characterization of the mentioned cryo-materials for adiabatic demagnetization at very low temperature whose efficiency depends on the $\partial S_m/\partial T|_{T\to 0}$ slope (i.e. $C_m/T|_{T\to 0}$) and the effect of external magnetic field [2,9].

As shown in Fig. 5 there are three distinct possibilities for the entropy to extrapolate to zero at $T = 0$. They can be unambiguously classified through their different $S_m(T)$ curvature, i.e. $\partial^2 S_m/\partial T^2$. The faster condensation of degrees of freedom occurs in the magnetically ordered phases which are described by a positive ($\partial^2 S_m/\partial T^2 > 0$) curvature below their ordering temperature $T_{MO}$.

The members of the $C_m/T|_{T\to 0}$ 'plateau' group follow a linear $S_m|_{T\to 0}$ thermal dependence ($\partial^2 S_m/\partial T^2 = 0$) below the *bottleneck* temperature $T^*$. Although his behavior is also shown by Fermi Liquids (FL) and simple metals, their band character cannot be naïvely extrapolated to the 'plateau' group. This is because at $T = T^*$ these VHF systems show an evident change of regime, which is not observed in FL systems which enter into the $C_m/T|_{T\to 0} = const.$ regime in a continuous way. In other words, the difference arises from the fact that for normal FL the characteristic temperature only represents a scale of energy but not a change of regime. Nevertheless, the mentioned formation of a coherent ground state in $YbCu_{5-x}Au_x$ [10], $PrInAg_2$ [4] or $CeNi_9Ge_4$ [1] opens the question about a possible very narrow band formation below $T^*$.

The third possibility is fulfilled by NFL systems with a $C_m/T \propto -\ln(T/T_0)$ dependence because they approach $T = 0$ with a negative $\partial^2 S_m/\partial T^2 < 0$ curvature. Contrary to the power law $C_m/T \propto 1/T^Q$ divergence, NFL type behavior extrapolate to $S_m = 0$ for $T \to 0$ together with $C_m|_{T\to 0} = 0$. Another characteristic of this $S_m(T)$ behavior is that some of them (e.g. $CeNi_{8.95}Co_{0.05}Ge_4$ and $Yb_{0.81}Sc_{0.19}Co_2Zn_{20}$) show the highest measured $C_m/T$ values, with associated highest $\partial S_m/\partial T$ slopes at low temperature. It is worth noting that the $C_m/T = -\ln(T/T_0)$ decay is softer than the $1/T^Q$ one and, consequently, the $S_m(T)$ increase is more moderated in NFL than in VHF. Most of experimental examples for NFL behavior correspond to Ce- or Yb-based systems tuned to a QCP and therefore they are affected by a relevant Kondo screening effect.

## 3. Conclusions

As it was shown, magnetic systems which are not able to develop an ordered phase undergo an *entropy-bottleneck* produced by the third law condition that $S_m|_{T\to 0} \geq 0$. This scenario is observed in compounds showing a $C_m/T \propto 1/T^Q$ power law above a characteristic temperature $T^*$ (i.e. within their paramagnetic regime) because the divergent thermal dependence would exceed the limited amount of degrees of freedom 'Rln2' for of a doublet GS. The change of regime, induced by thermodynamic constraints and not by standard magnetic interactions, is reflected in the $S_m(T)$ dependence as an upwards deviation from the trajectory extrapolated from the $T > T^*$ region.

The value of $T^*$ is established by the $C_m = S_m$ equality extracted from the point where $S_m/T$ coincides with $\partial S_m/\partial T$. From this condition it can be deduced that the case of VHF, that show a $C_m/T|_{T\to 0} =$ const. 'plateau', corresponds to a zero value in the Planck's potential. The difference with the ordered systems becomes evident once respective $S_m|_{T>T^*}$ and $S_m|_{T<T^*}$ trajectories are compared, because in not ordered VHF systems $S_m(T^*)$ corresponds to an inflection point whereas in magnetically ordered compounds $S_m(T_{MO})$ is associated to a second order transition where the change of slope is related to a $\Delta C_m$ jump.

In the case of NFL systems, the $C_m = S_m$ equality occurs at $T = 0$. As a consequence they may show the greatest negative curvature in the $S(T)$ dependence when approaching $T = 0$. This property, together with the sensitivity to external magnetic fields, becomes relevant for the search of proper cryo-materials in the sub-kelvin range.

## Acknowledgments

The author is grateful to I. Curlik, M. Deppe, E. Bauer, M. Giovannini, T. Gruner, J.P. Kappler, H. Michor, E-W Scheidt, I. Zeiringer and A. Strydom for allowing to access to original results. This work was partially supported by projects UNCuyo 06/C520 and CONICET PIP-2013-100576.

## References

[1] C. Gold, M. Uffinger, M. Herzinger, G. Eickerling, W. Scherer, H. Michor, E.-W. Scheidt, J. Alloy. Compd. 523 (2012) 61.
[2] T. Gruner, D. Jang, A. Steppke, M. Brando, F. Ritter, C. Krellner, C. Geibel, J. Phys.: Condens. Matter 26 (2014) 485002.
[3] H.v. Löhneysen, F. Huster, S. Mock, A. Neubert, T. Pietrus, M. Sieck, O. Stockert, M. Waffenschmidt, Phys. B 230–232 (1997) 550.
[4] A. Yatskar, W.P. Beyermann, R. Movshovich, P.C. Canfield, Phys. Rev. Lett. 77 (1996) 3637.
[5] Z. Fisk, P.C. Canfield, W.P. Beyermann, J.D. Thompson, M.F. Hundley, H.R. Ott, E. Felder, M.B. Maple, M.A. Lopez de la Torre, P. Visani, C.L. Seamanet, Phys. Rev. Lett. 67 (1991) 3310.
[6] I. Curlik, M. Giovannini, J.G. Sereni, M. Zapotokova, S. Gabani, M. Reiffers, Phys. Rev. B 90 (2014) 224409.
[7] M.S. Torikachvili, S. Jia, E.D. Mun, S.T. Hannahs, R.C. Black, W.K. Neils, D. Martien, S.L. Bud'ko, P.C. Canfield, PNAS 104 (2007) 9960.
[8] D. Jang, T. Gruner, A. Steppke, K. Mistsumoto, C. Geibel, M. Brando, Matur. Commun. (2015) (ncomms9680).
[9] Y. Tokiwa, B. Piening, H.S. Jeevan, S.L. Bud?ko, P.C. Canfield, P. Gegenwart, Sci. Adv. 2 (2016) e1600835.
[10] K. Yoshimura, T. Kawabata, N. Sato, N. Tsujii, T. Terashima, C. Terakura, G. Kido, K. Kosuge, J. Alloy. Compd. 317 (2001) 465.
[11] P. Carretta, R. Pasero, M. Giovannini, C. Baines, Phys. Rev. B 79 (2009) 020401 (R).
[12] This $C_m(T)/T$ data were measured on a $Dy_2Ti_2O_7$ single crystal provided by S. Grigera, University of La Plata, Argentina.
[13] Z. Hiroi, K. Matsuhira, M. Ogata, J. Phys. Soc. Jpn. 72 (2003) 304545.
[14] J.G. Sereni, Phenomenologic function used to describe $C_m(T)/T$ power law dependencies, J. Low Temp. Phys. 147 (2007) 147.
[15] J.G. Sereni, J. Low. Temp. Phys. 179 (2015) 126.
[16] L. Peyker, C. Gold, W. Scherer, H. Michor, E.-W. Scheidt; J.Phys.:Conference Series 273 (2010) 012049.
[17] R. Higashinaka, H. Fukazava, K. Deguchi, Y. Maeno, J. Phys. Soc. Jpn. 73 (2004) 2845.
[18] J.G. Sereni, M. Giovannini, M. G-Berisso, F. Gastaldo, J. Phys.: Condens. Matter 28 (2016) 475–601.
[19] M. Planck, in Treatise on Thermodynamics, Dover Publications, Inc., 1926.