Absence of Magnetic Order in $Yb_3Ga_5O_{12}$: Relation between Phase Transition and Entropy in Geometrically Frustrated Materials

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From muon spin relaxation spectroscopy experiments, we show that the sharp peak (λ-type anomaly) detected by specific heat measurements at 54 mK for the ytterbium gallium garnet compound, $Yb_3Ga_5O_{12}$, does not correspond to the onset of a magnetic phase transition, but to a pronounced building up of dynamical magnetic pair correlations. Beside the λ anomaly, a broad hump is observed at higher temperature in the specific heat of this garnet and other geometrically frustrated compounds. Comparing with other frustrated magnetic systems we infer that a ground state with long-range order is reached only when at least $1/4 - 1/3$ of the magnetic entropy is released at the λ transition.

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A magnetic phase transition to a long-range order occurs at low temperature for most crystallographically ordered compounds containing a three-dimensional lattice of magnetic ions. Its classical signature is a sharp anomaly in the magnetic specific heat (SH) at temperature T_λ which corresponds to the phase transition temperature; see, e.g., Ref. [1]. In this Letter, for convenience, we label such anomaly a λ anomaly although it may not have all of the properties attributed to such an anomaly [2].

However, for some particular lattice structures, the long-range magnetic ordering of the magnetic ions may be impeded by their geometric arrangement which gives rise to the frustration of their magnetic interactions [3,4]. Most of the experimental studies focus nowadays on pyrochlore and gallium garnet compounds, $R_2T_2O_7$ and $R_3Ga_5O_{12}$, respectively. R denotes a rare earth atom and T a transition element. The R ions are arranged on a motif of corner sharing tetrahedra for the pyrochlore structure. In the garnet case, the R atoms form two interpenetrating, noncoplanar, corner sharing triangular sublattices. For an experimental review, see, e.g., Ref. [5].

The results from SH measurements are particularly intriguing. Although $|\theta_{\mathrm{CW}}|/T_\lambda \gtrsim 1$, where θ_{CW} is the Curie-Weiss temperature, long-range order may not be present below T_λ.

For example, let us review data on pyrochlore compounds. According to SH, $Gd_2Ti_2O_7$ has two magnetic phase transitions at 1 K and ~0.75 K and no defined structure in the SH data is observed above 1 K [6]. The detection of magnetic Bragg reflections from neutron scattering at 50 mK shows that a magnetic structure is established [7]. Similarly, $Gd_2Sn_2O_7$ has a large λ anomaly in SH and Mössbauer spectroscopy [8] and muon spin relaxation (μSR) [9] are consistent with the presence of long-range ordering. A λ anomaly is detected at ~1.2 K for $Er_2Ti_2O_7$ [10] and long-range order is observed at low temperature [11]. For $Yb_2Ti_2O_7$ a λ anomaly is found at $T_\lambda \simeq 0.21$ K [10] but there are no long-range magnetic correlations below T_λ but rather dynamical hysteretic short-range correlations [12]. We note that beside the λ peak, a broad peak centered near 2 K is present in SH. In the popular spin-ice systems $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$, only a broad anomaly is present in SH [13] and at low temperature the magnetic moments are frozen with no long-range order [14,15].

Concerning the garnets, only a broad SH peak is detected at low temperature for $Gd_3Ga_5O_{12}$ [16]. This compound does not display any long-range order [17]. $Dy_3Ga_5O_{12}$ displays an SH anomaly at $T_\lambda \simeq 0.37$ K, overlapping with a broad peak [18]. Neutron scattering results show the presence of a long-range magnetic order below T_λ [19]. Finally, while a λ anomaly is found for $Yb_3Ga_5O_{12}$ at $T_\lambda = 54$ mK [20], no information is available in the literature about the existence of a short- or long-range magnetic order. We note that a relatively large SH hump is also present, centered at ~0.2 K.

Since no λ anomaly is present in the spin-ice systems and in $Gd_3Ga_5O_{12}$ we shall not consider these systems any longer. To gain further understanding of the relationship between entropy and magnetic correlations in $Yb_3Ga_5O_{12}$, we performed μSR measurements on this system. Here we assume, that the measured SH corresponds to magnetic dipole moment degrees of freedom and not to another exotic order parameter [21].

In the garnet lattice (space group $Ia\bar{3}d$), the crystal field acts on the $^2F_{7/2}$ state of a Yb^{3+} ion to leave a well-isolated ground-state Kramers doublet and three closely grouped excited doublets having an average energy corresponding to $\Delta_{\mathrm{ave}}/k_{\mathrm{B}} \simeq 850$ K [22]. In a good approximation, the ground state of Yb^{3+} ions diluted in $Y_3Ga_5O_{12}$ is described by an effective spin $S' = 1/2$ with an isotropic g factor, $g = 3.43$ [23,24]. The same

description of Yb^{3+} in $Yb_3Ga_5O_{12}$ is expected to be valid. This is supported by the electronic entropy variation below 1 K which is very close to $R\ln 2$ [20], as expected for a doublet. R is the gas constant. From the measured g factor and bulk magnetization [20], the mean value of the Yb^{3+} magnetic moment at low temperature is found to be $\sim 1.7\mu_B$. The interionic interaction is essentially antiferromagnetic as shown from the susceptibility above T_λ which is lower than that extrapolated from high temperature for a Curie-Weiss behavior [20]. From the position of the maximum of the bump of the SH an estimate for this interaction strength corresponds to at least 0.2 K. The antiferromagnetic nature of the interactions together with the crystallographic structure leads to frustration.

A sample was prepared by heating the constituent oxides to 1100 °C 4 times with intermediate grindings. Its quality was checked by x-ray diffraction and susceptibility measurements. Zero-field μSR measurements were performed at the ISIS and PSI muon facilities covering the temperature range from 21 mK to 290 K. Additional spectra were recorded with a longitudinal field.

^{170}Yb Mössbauer spectroscopy experiments [25] performed between 36 mK and 4.2 K show no resolved hyperfine structure at any temperature including below T_λ as depicted in the inset of Fig. 1. This means that the moments fluctuate at a frequency larger than $\sim 300\ \mu s^{-1}$ down to 36 mK. This also indicates the absence of magnetic correlations either short or long range.

We now present zero-field μSR results. The technique consists of implanting polarized (along direction Z) muons into a specimen and monitoring $P_Z^{\rm exp}(t)$ which is the evolution of the muon ensemble polarization projected onto direction Z [26]. The quantity actually measured is the so-called asymmetry corresponding to $a_0 P_Z^{\rm exp}(t)$, where $a_0 \simeq 0.24$.

For a paramagnet, $P_Z^{\rm exp}(t)$ tracks the dynamics of the magnetic field at the muon site, $\mathbf{B}_{\rm loc}$, reflecting the dynamics of the electronic moments. In the fast fluctuation or motional narrowing limit, $P_Z^{\rm exp}(t)$ takes an exponential form characterized by a relaxation rate, λ_Z. A stochastic approach to relaxation in zero field leads to the relation $\lambda_Z = 2\gamma_\mu^2 \Delta_{\rm ZF}^2 \tau_c$, assuming a single correlation time, τ_c, for the magnetic moment dynamics. $\Delta_{\rm ZF}$ is the standard deviation of the components of $\mathbf{B}_{\rm loc}$ and γ_μ the muon gyromagnetic ratio ($\gamma_\mu = 851.615$ mrad s^{-1} T^{-1}). The motional narrowing limit is valid if $\gamma_\mu \Delta_{\rm ZF} \tau_c \ll 1$.

Two examples of μSR spectra are shown in Fig. 1. All the spectra were satisfactorily fitted to an exponential function. The temperature dependence of λ_Z is shown in Fig. 2. Since there is no qualitative change in $P_Z^{\rm exp}(t)$ and since λ_Z increases monotonously as the temperature is lowered, there is neither long-range nor short-range magnetic order in $Yb_3Ga_5O_{12}$. This means that the specific heat anomaly at T_λ does not correspond to the onset of a conventional phase transition, in agreement with the ^{170}Yb Mössbauer results. This is our first result.

The fact that we observe an exponential relaxation function below T_λ is another important point. It implies that we are in the fast fluctuation limit (we shall check this quantitatively below) and therefore the Yb^{3+} moments continue to fluctuate rapidly down to the lowest temperature investigated. This behavior is very different from that in $Yb_2Ti_2O_7$ where the moments abruptly slow down below T_λ where they are quasistatic [12].

We now comment and interpret the shape of $\lambda_Z(T)$.

As for nuclear magnetic resonance [27], λ_Z can be expressed in terms of the static wave vector dependent

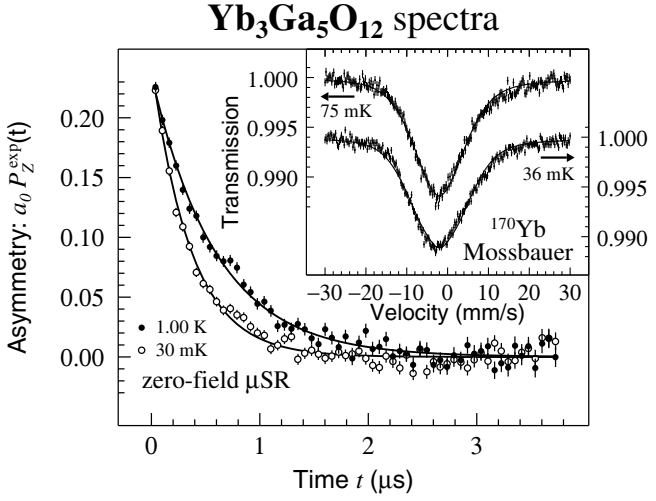

FIG. 1. Zero-field μSR spectra recorded for $Yb_3Ga_5O_{12}$, both above and below T_λ. The solid lines in the μSR spectra are the results of fits to exponential relaxation functions as explained in the text. In the inset, ^{170}Yb Mössbauer reproduced from Ref. [25]. These data show the absence of long- or short-range correlations below T_λ.

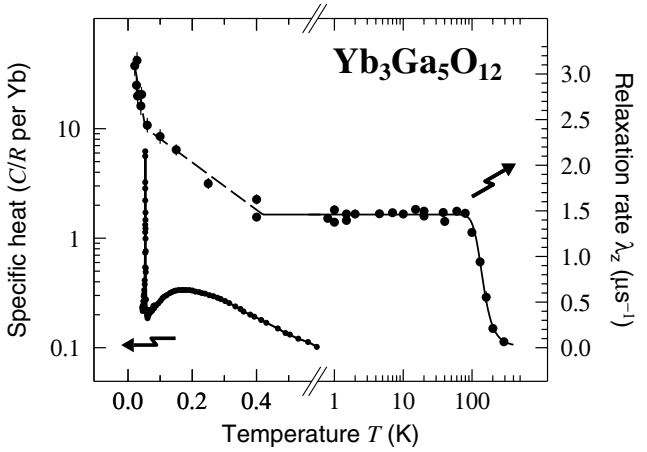

FIG. 2. Zero-field muon spin-lattice relaxation rate, λ_Z, versus temperature measured for $Yb_3Ga_5O_{12}$. The solid line is the result of a fit to a model explained in the main text. The two straight dashed lines for $T \leq 0.4$ K down to 21 mK are guides to the eye. The specific heat (from Ref. [20]) of $Yb_3Ga_5O_{12}$ is also reproduced. A marked change of slope in $\lambda_Z(T)$ occurs at $T_\lambda = 54$ mK.

susceptibility, $\chi(\mathbf{Q})$, and linewidth of the quasielastic peak of the imaginary component of the dynamical susceptibility, $\Gamma(\mathbf{Q})$. These two functions are assumed to be scalar, consistent with the quasi-isotropic nature of the Kramers ground-state doublet. Following Ref. [28] we write

$$\lambda_Z = \frac{\mu_0 \gamma_\mu^2}{16\pi^2} k_B T \int C(\mathbf{Q}) \frac{\chi(\mathbf{Q})}{\Gamma(\mathbf{Q})} \frac{d^3\mathbf{Q}}{(2\pi)^3}. \quad (1)$$

μ_0 is the permeability of free space and k_B the Boltzmann constant. The term $C(\mathbf{Q})$ accounts for the interaction of the muon spin with the Yb^{3+} effective spins. The integration is over the first Brillouin zone.

For a Heisenberg magnet at high temperature, i.e., if the thermal energy is larger than the exchange energy, the $\mathbf{Q}$ dependence of $\chi(\mathbf{Q})$ becomes negligible (see, e.g., Ref. [29]) and it is simply given by the Curie law. Since $\Gamma(\mathbf{Q})$ is temperature independent in the same limit [29], we deduce that λ_Z should be temperature independent. This is effectively observed for $0.4 \leq T \leq 80$ K.

However, above 80 K, $\lambda_Z(T)$ decreases steadily as the sample is heated. Such a behavior is sometimes associated with muon diffusion, but it would be quite unusual in an insulating oxide. In fact the decrease of λ_Z is due to the relaxation of the Yb^{3+} magnetic moments resulting from an Orbach process, i.e., a two-phonon real process with an excited crystal-field level as intermediate [30,31]. A global fit is achieved with the formula $\lambda_Z^{-1} = A + B_{me} \exp[-\Delta_e/(k_B T)]$. Δ_e is the energy of the excited crystal-field level involved. $A \simeq \lambda_Z^{-1}$ when λ_Z saturates at low temperature (but still $T > 0.4$ K). The constant B_{me} models the magnetoelastic coupling of the Yb^{3+} spin with the phonon bath. The result of the fit for $0.4 \leq T \leq 290$ K is shown in Fig. 2. Taking $\Delta_e/k_B = \Delta_{ave}/k_B = 850$ K, we get $A = 0.69(2)$ μs and $B_{me} = 250(70)$ μs. Combining the value of λ_Z in the range $0.4 < T < 80$ K and the value $\tau_c \sim 38$ ps obtained from perturbed angular correlation and Mössbauer data in the same temperature interval [25], we compute $\Delta_{ZF} \simeq 0.16$ T which is of the expected magnitude. For comparison $\Delta_{ZF} \simeq 0.08$ T was found for $Yb_2Ti_2O_7$ above T_λ [32].

Information relevant to the influence of the frustrated nature of the magnetic interactions in $Yb_3Ga_5O_{12}$ is obtained from $\lambda_Z(T)$ at low temperatures. As shown in Fig. 2, λ_Z starts to deviate at $\sim$0.4 K from the behavior expected for the Heisenberg Hamiltonian in the high-temperature limit. As we cool down the sample, we first observe a mild linear increase of λ_Z, with slope $-2.6(3)$ $\mu s^{-1} K^{-1}$, followed by a sharp increase below T_λ with slope $-21(7)$ $\mu s^{-1} K^{-1}$.

In the temperature range $T_\lambda < T < 0.4$ K, we note that the broad SH peak centered at $\sim$0.2 K covers the temperature regime where $\lambda_Z(T)$ varies slowly, suggesting that both features reflect the same physics. Since there are no excited crystal-field energy levels at low energy, the hump cannot be of a Schottky type. This extra SH reflects short-range correlations among groups of spins; see, e.g., Ref. [1]. This means that the spin dynamics is wave vector dependent below $\sim$0.4 K. This dependence is expected to generate a mild increase of λ_Z as shown by the explicit computation of Paja and co-workers [33] for a simple model.

Now we turn our attention to the region $T < T_\lambda$. Being in an interstitial site, the muon spin can be strongly influenced by magnetic pair correlations. In contrast, since a ^{170}Yb Mössbauer nucleus is embedded in a Yb atom which is magnetic, it is mainly sensitive to the self-correlations. Taking into account that the dynamics measured by Mössbauer spectroscopy is not wildly different above and below T_λ [25], we infer that the sharp increase of λ_Z occurring right below T_λ is the signature of the building up of magnetic pair correlations. Down to the lowest temperature, the μSR spectra have been recorded in the motional narrowing limit, since we compute $\gamma_\mu \Delta_{ZF} \tau_c \simeq 0.02 \ll 1$ at low temperature, taking as an estimate for τ_c the hyperfine field correlation time from Mössbauer ($\sim$0.3 ns) and computing $\Delta_{ZF} \simeq 0.08$ T from the relation $\lambda_Z = 2\gamma_\mu^2 \Delta_{ZF}^2 \tau_c$. Therefore, the exponential form of the relaxation is fully justified.

An experimental estimate for τ_c can in principle be obtained from the analysis of the field dependence of λ_Z assuming that the properties of the system are not modified by an external field. In the case of $Yb_3Ga_5O_{12}$ we have found that a field as low as 0.3 T has a strong influence, increasing rather than quenching λ_Z. We conclude that the field influences the system: this is not completely astonishing recalling that a field of 0.7 T induces a phase transition for the isomorphous compound $Gd_3Ga_5O_{12}$ [16].

$Yb_3Ga_5O_{12}$ is therefore a second system with frustrated magnetic interactions, after $Yb_2Ti_2O_7$, where no long-range order is found below T_λ. In the pyrochlore a sharp first-order transition appears in the fluctuation rate of the magnetic moments and below T_λ they continue to fluctuate slowly (in the megahertz range) at a temperature independent frequency. In the garnet we have a new scenario: the fluctuations are still rapid below T_λ and no abrupt change in their frequency is observed. Only dynamical short-range correlations build up. The continuous rise of λ_Z is magnetic in origin and therefore excludes a dimer phase to be formed below T_λ.

Among the different frustrated pyrochlores and garnets with a λ peak in SH that we have considered at the beginning of this Letter, i.e., $Gd_2Ti_2O_7$, $Gd_2Sn_2O_7$, $Er_2Ti_2O_7$, $Yb_2Ti_2O_7$, $Dy_3Ga_5O_{12}$, and $Yb_3Ga_5O_{12}$, some of them order and others do not. One can tentatively find a condition for a magnetic order to be present. For all these compounds the variation of magnetic entropy at low temperature, say, below $\sim$10 K, is close to the expected value deduced from the number of electronic degrees of freedom. This is $R \ln 8$ for the Gd based compounds and $R \ln 2$ for the others. Inspecting Refs. [6,8,10,12,18–20], the fraction of the total entropy frozen at T_λ is roughly

60% for $Er_2Ti_2O_7$ and $Dy_3Ga_5O_{12}$, 40% for $Gd_2Sn_2O_7$, and 35% for $Gd_2Ti_2O_7$, whereas it is only $\simeq 20\%$ for $Yb_2Ti_2O_7$ and $Yb_3Ga_5O_{12}$. Therefore we estimate that a long-range magnetic order is present only when at least $1/4 - 1/3$ of the magnetic entropy is released at T_λ.

While the entropy change at the λ anomaly temperature is about the same for both $Yb_3Ga_5O_{12}$ and $Yb_2Ti_2O_7$, the Kramers ground-state doublet is approximately isotropic for the former and strongly anisotropic for the latter. This suggests that a high magnetic anisotropy impedes the system from exploring different configurations, leading to an abrupt slowing down of the correlations. Δ_{ZF} is reduced by a factor $\simeq 14$ [12,32] when crossing T_λ from above for $Yb_2Ti_2O_7$ whereas this reduction is much less ($\lesssim 2$) for $Yb_3Ga_5O_{12}$. This is again consistent with the anisotropy difference between both systems: we expect Δ_{ZF} to be small if the magnetic moments are confined to specific orientations.

In conclusion, according to wisdom, a λ-type anomaly is indicative of a second order phase transition at T_λ for a three-dimensional system. However, due to the presence of frustrated interactions, only dynamical short-range correlations build up below T_λ in $Yb_3Ga_5O_{12}$. By comparison with results from other three-dimensional frustrated systems, we infer that the long-range order of the order parameter does not occur if a too large fraction of the entropy is released at a broad bump located above T_λ. The anisotropy of the system favors a freezing of the magnetic correlations.

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[1] A. Morrish, *The Physical Principles of Magnetism* (Wiley & Sons, New York, 1965).
[2] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Clarendon Press, Oxford, 1971).
[3] J. Villain, Z. Phys. B **33**, 31 (1979).
[4] *Systems with Competing Interactions*, edited by H. T. Diep (World Scientific, Singapore, 1994).
[5] A. P. Ramirez, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, New York, 2001), Vol. 13.
[6] A. P. Ramirez, B. S. Shastry, A. Hayashi, J. J. Krajewski, D. A. Huse, and R. J. Cava, Phys. Rev. Lett. **89**, 067202 (2002).
[7] J. D. M. Champion, A. S. Wills, T. Fennell, T. Bramwell, J. S. Gardner, and M. A. Green, Phys. Rev. B **64**, 140407 (2001).
[8] P. Bonville, J. A. Hodges, M. Ocio, J. P. Sanchez, P. Vulliet, S. Sosin, and D. Braithwaite (unpublished).
[9] A. Yaouanc, P. Dalmas de Réotier, P. Bonville, J. A. Hodges, P. C. M. Gubbens, and C. Baines (unpublished).
[10] H. W. J. Blöte, R. F. Wielinga, and W. J. Huiskamp, Physica (Utrecht) **43**, 549 (1969).
[11] J. D. M. Champion *et al.*, Phys. Rev. B **68**, 020401(R) (2003).
[12] J. A. Hodges *et al.*, Phys. Rev. Lett. **88**, 077204 (2002).
[13] A. P. Ramirez, A. Hayashi, R. J. Cava, R. Siddharthan, and B. S. Shastry, Nature (London) **399**, 333 (1999).
[14] M. J. Harris, S. T. Bramwell, D. F. McMorrow, T. Zeiske, and K. W. Godfrey, Phys. Rev. Lett. **79**, 2554 (1997).
[15] S. T. Bramwell and M. J. P. Gingras, Science **294**, 1495 (2001).
[16] P. Schiffer, A. P. Ramirez, D. A. Huse, and A. J. Valentino, Phys. Rev. Lett. **73**, 2500 (1994).
[17] O. A. Petrenko, C. Ritter, M. Yethiraj, and D. M. Paul, Phys. Rev. Lett. **80**, 4570 (1998).
[18] J. Filippi, J. C. Lasjaunias, B. Hebral, J. Rossat-Mignod, and F. Tcheou, J. Magn. Magn. Mater. **15–18**, 527 (1980).
[19] J. Filippi, Ph.D. thesis, Université Scientifique et Médicale de Grenoble and Institut National Polytechnique de Grenoble, 1981 (unpublished).
[20] J. Filippi, J. C. Lasjaunias, B. Hebral, J. Rossat-Mignod, and F. Tcheou, J. Phys. C **13**, 1277 (1980).
[21] J. A. Paixão, C. Detlefs, M. J. Longfield, R. Caciuffo, P. Santini, N. Bernhoeft, J. Rebizant, and G. H. Lander, Phys. Rev. Lett. **89**, 187202 (2002).
[22] R. A. Buchanan, K. A. Wickersheim, J. J. Pearson, and G. F. Herrmann, Phys. Rev. **159**, 245 (1967).
[23] J. W. Carson and R. L. White, J. Appl. Phys. **31**, 53S (1960).
[24] W. P. Wolf, M. Ball, M. T. Hutchings, M. J. M. Leask, and A. F. G. Wyatt, J. Phys. Soc. Jpn., Suppl. B-1 **17**, 443 (1962).
[25] J. A. Hodges, P. Bonville, M. Rams, and K. Królas, J. Phys. Condens. Matter **15**, 4631 (2003).
[26] P. Dalmas de Réotier and A. Yaouanc, J. Phys. Condens. Matter **9**, 9113 (1997).
[27] T. Moriya, Prog. Theor. Phys. **28**, 371 (1962).
[28] A. Yaouanc, P. Dalmas de Réotier, and E. Frey, Phys. Rev. B **47**, 796 (1993).
[29] S. W. Lovesey, *Theory of Neutron Scattering from Condensed Matter* (Oxford University Press, Oxford, 1984), Vol. 2.
[30] R. Orbach, Proc. Phys. Soc. London Sect. A **264**, 458 (1961).
[31] A Raman process can be theoretically effective but it does not fit the data.
[32] A. Yaouanc, P. Dalmas de Réotier, P. Bonville, J. A. Hodges, P. C. M. Gubbens, C. T. Kaiser, and S. Sakarya, Physica (Amsterdam) **326B**, 456 (2003).
[33] A. Paja, H. Figiel, and P. Mietniowski, J. Phys. Condens. Matter **14**, 9029 (2002).