Magnetic Field Induced Transitions from Spin Glass to Liquid to Long Range Order in a 3D Geometrically Frustrated Magnet

Y. K. Tsui,[1] C. A. Burns,[2] J. Snyder,[1] and P. Schiffer[1]
[1]*Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556*
[2]*Department of Physics, Western Michigan University, Kalamazoo, Michigan 49008*
(Received 17 December 1998)

Gadolinium gallium garnet, $Gd_3Ga_5O_{12}$, has an extraordinary low temperature phase diagram including a spin glass phase near $H = 0$ T, an antiferromagnetic (AFM) phase for $0.7 \leq H \leq 1.4$ T, and, at intermediate fields, an apparent spin-liquid state without long range order. We have characterized the intermediate field (IF) state through heat capacity, thermal conductivity, and magnetocaloric measurements. Our results indicate that the IF phase is distinct from the spin glass, and that the phase boundary between the AFM and IF phases has a distinct minimum at $T \sim 0.18$ K, in analogy to the minimum in the melting curve of ^{4}He. [S0031-9007(99)08981-4]

PACS numbers: 75.30.Kz, 75.50.Ee

There has been much recent interest in the study of geometrically frustrated antiferromagnets [1], in which the geometry of the lattice results in frustration of the antiferromagnetic exchange interaction. Such materials are characterized by the absence of long range order at temperatures well below the Curie-Weiss temperature ($|\Theta_{CW}|$), and have highly unusual low temperature properties [1–9]. One such frustrated magnet is $Gd_3Ga_5O_{12}$ (gadolinium gallium garnet or GGG), in which the magnetic Gd ions are on three dimensional corner-sharing triangular sublattices, which results in geometrical frustration of the antiferromagnetic (AFM) nearest neighbor exchange interactions [10,11] ($\Theta_{CW} \sim -2$ K) and an unusual phase diagram (Fig. 1 inset). At low fields, previous thermodynamic studies indicate that the ground state of GGG is a spin glass ($T_g \sim 150$ mK) [7], although recent neutron scattering data suggest that the spin glass state does not involve all of the spins [4]. At fields between 0.7 and 1.4 T the ground state is a long range order AFM state with $T_N(\max) \sim 350$ mK [3,5–7]. The nature of the ground state at intermediate fields shows no evidence of any sort of spin ordering upon cooling from the high temperature paramagnetic state. This state is apparently a homogeneous three dimensional spin liquid in which the spin interactions are much stronger than the ambient thermal energies, and yet the spins remain fluctuating at low temperatures without long range correlations [12].

In this Letter we characterize the low temperature spin state of GGG in the intermediate field (IF) regime through the thermal properties of a high-quality single crystal of GGG. Our data show a clear upper field boundary of the spin glass phase of GGG, demonstrating that the IF phase is distinct from the spin glass phase. We also find a minimum in the IF/AFM phase boundary, indicating that the "disordered" IF state close to the phase boundary has lower magnetic entropy than the ordered AFM state, and this finding is confirmed by measurements of the latent heat at the transition. The minimum in the phase boundary is analogous to that in the melting curve of ^{4}He and represents a novel transition between a spin liquid at intermediate fields and a long range ordered spin solid in the AFM state.

In order to characterize the IF phase, we measured the thermal conductivity, $\kappa(H,T)$, and the heat capacity, $C(H,T)$ [9]. Our heat capacity data (see Ref. [9] for a complete data set) agree well with previous less detailed measurements [3]. There are no ordering features in $C(T)$ for $H \lesssim 0.7$ T, down to the lowest temperature of this experiment ($\sim$65 mK). At fields close to zero, the quotient $C(T)/T$ (representative of the density of states) drops rapidly below $\sim$90 mK. This decline in $C(T)/T$, is reminiscent of the low temperature behavior of the

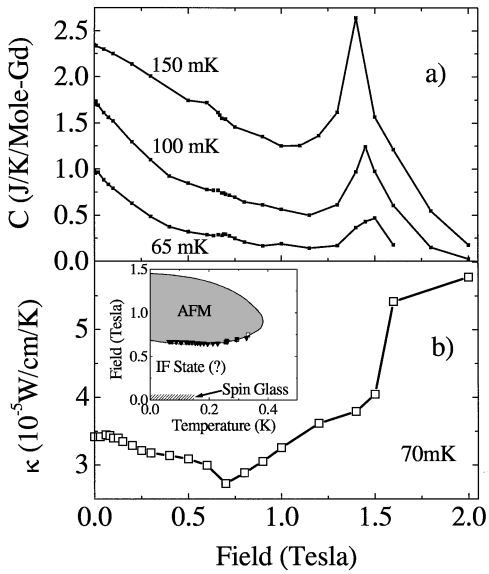

FIG. 1. The (a) specific heat (C) and (b) thermal conductivity (κ) of GGG vs applied field at low temperatures and low fields. The inset shows the low temperature phase diagram of GGG including the spin glass, IF, and AFM long range ordered phases [3]. The solid down triangles correspond to $T_s(H)$ data, and open squares correspond to peaks in new $C(T)$ data.

 0031-9007/99/82(17)/3532(4)$15.00

frustrated kagomé compound $SrCr_{9p}Ga_{12-9p}O_{19}$, in which the low temperature state is spin liquid-like [8]. Our $C(T)$ data do display sharp long range order (LRO) peaks at the AFM phase high-field boundary, in agreement with previous results [3,6]. In order to study how the applied field affects the thermodynamics, we plot $C(H)$ at several temperatures as shown in Fig. 1a. In the low field and low temperature regime, $C(H)$ decreases with H, suggesting that the density of states of the spin fluctuations is also decreasing with H. The $C(H)$ curves show features at the transitions to and from the AFM state at 0.7 and 1.4 T, respectively. The asymmetry of the features reflects the rather different natures of the two phase boundaries since the upper boundary is second order with a relatively large $|dH_c/dT|$ [3], while the lower boundary is first order and almost flat as discussed below.

The thermal conductivity data compare well to the previous zero-field measurements of Daudin *et al.* [13]. We find that $\kappa(H)$ displays features corresponding to the AFM phase boundaries and then rises and saturates at high fields, with $\kappa(H \geq 5\ \mathrm{T})/\kappa(0) \sim 2.5$ for $T \leq 300$ mK [9]. Since the magnetization is saturated for $H \geq 3$ T, spins excitations should not affect thermal conduction at high fields, and we thus conclude that phonons are the predominant heat carriers despite the heat capacity being primarily due to spin fluctuations [14]. Confirming this conclusion, we find $\kappa(T) \sim T^3$ as expected for phonons [9], and the magnitude of $\kappa(T)$ is consistent with Debye model predictions. Since thermal conduction is through phonons, the features at low fields must be due to scattering of the phonons by spin excitations. For $0.1 < H < 0.7$ T, the IF phase, $\kappa(H)$ decreases with fields at low temperatures, implying an increase in spin-phonon scattering. This is surprising since $C(H)$ in this region shows a decrease in the density of state of the spin excitations—suggesting that the cross section for spin excitation scattering increases strongly with field.

An unanswered question from previous low temperature studies of GGG is whether the IF spin state ($0.1 \leq H \leq 0.7$ T) is in fact distinct from the spin glass state. The previously observed maximum in $\chi_{\mathrm{ac}}(H = 0)$ [7] corresponding to the spin glass transition was suppressed for $H \gtrsim 0.05$ T [7], indicating an approximate upper field bound of the spin glass phase; however, no feature was observed in $\chi(H)$ [15]. In Fig. 2c we show $C(H)$ and $\kappa(H)$ at low fields. For $T < T_g$ we find that $C(H)$ is almost constant when $H \leq 0.02$ T, then it decreases with field almost linearly, while $\kappa(H)$ shows a broad peak at $\sim$0.1 T—both suggestive of a boundary between the spin glass and IF phases.

To further characterize the evolution of the spin state with field, we performed magnetocaloric measurements using our calorimeter to measure the temperature of the sample, $T_s(H)$, during quasiadiabatic field sweeps. We zero-field cooled the sample and then measured $T_s(H)$ while sweeping the field slowly, $0 \rightarrow 0.2\ \mathrm{T} \rightarrow 0$. For

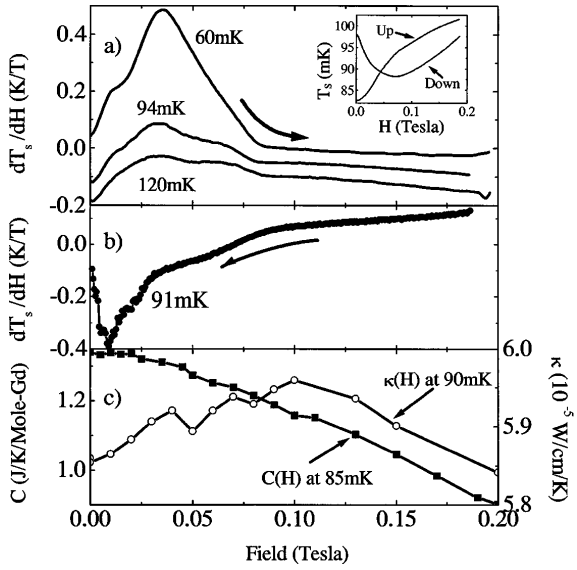

FIG. 2. The field dependence of several properties of GGG in the low field region. (a) The sweeping up data of dT_s/dH at different temperatures. The 94 and 120 mK curves have been off set for clarity. The inset shows the typical field dependence of $T_s(H)$ for both the sweeping up and down data. (b) Typical decreasing field measurements of dT_s/dH. (c) $\kappa(H)$ at 90 mK and $C(H)$ at 85 mK.

$H \leq 0.08$ T we observe an increasing $T_s(H)$ when the applied field is *either increased or decreased* (see inset to Fig. 2a). To illustrate the heating process more clearly, we plot dT_s/dH in Fig. 2a. On both increasing and decreasing field, dT_s/dH drops sharply at $\sim$0.08 T, indicating an upper bound to the heating, and this feature is unchanged when the rate of the field sweep is varied by a factor of 4. Since the heating occurs on both raising and lowering the field, it is not due to the demagnetization effect. We therefore attribute it to glassy irreversibility associated with the spin glass state of the sort observed in studies of the metallic spin glass *Au*Fe [16], in which the rate of heat flowing to or from the sample due to a change of the external field was measured. This irreversible heating may be pictured as an alteration of the spin glass energy landscape by the field during field sweeps. The continuous alteration of the landscape causes the system to irreversibly relax towards new equilibrium states, and energy is consequently released.

The feature in dT_s/dH at 0.08 T persists to $T \sim$ 800 mK, well above $T_g \sim 150$ mK determined from ac susceptibility and magnetization data. The persistence of glassiness to high temperatures is, however, consistent with the nonlinear susceptibility, χ_3 and the out-of-phase susceptibility χ'' data which show broad features at $\sim$0.5 K [7]. Taking the spin 7/2 of the Gd^{+3} ions to set the energy scale, 0.08 T is equivalent to $\mu_{\mathrm{Gd}}H/k_B \sim$ 380 mK, suggesting a correspondence with the features in χ_3 and χ''. In addition to the cutoff of heating at 0.08 T, dT_s/dH displays a peak at $\sim$0.033 T when $T \leq T_g$.

Since 0.033 T corresponds to $\mu_{\mathrm{Gd}} H/k_B \sim 160$ mK $\sim T_g$, this peak may correspond to the bulk spin glass transition.

The upper field boundary to the heating at 0.08 T suggests an upper field boundary for the spin glass phase, which in principle could be associated with either an Almeida-Thouless (AT) line or a Gabay-Toulouse (GT) line. However, as shown in Fig. 2a, the field where the irreversibility ends is almost temperature independent whereas AT and GT lines move to higher field as the temperature is reduced [17]. On the other hand, this feature allows us to define an upper boundary of the spin glass phase of GGG, which demonstrates that the intermediate field phase is a distinct spin state without glassy irreversibility and not simply a continuous extension of the spin glass state [15].

Perhaps one of the most intriguing results of earlier $\chi_{\mathrm{ac}}(H)$ measurements was that the two lowest temperature points on the low-field phase boundary of the AFM phase suggested that the boundary had a minimum at $T_{\mathrm{min}} \sim 200$ mK [3]. Such a minimum in the AFM/IF phase boundary would be highly unusual, indicating the disordered IF state for $T < T_{\mathrm{min}}$ was reentrant and possessed a higher degree of magnetic order than the long range ordered AFM phase. Our measurements of $C(T)$ at a field just below the AFM phase (0.66 T), however, did not indicate reentrance, perhaps due to the long relaxation time in this system. We then examined quasiadiabatic sweeps of $T_s(H)$ (see Fig. 3) across the boundary. These data indicated a transition to long range order at critical field, H_c, which is plotted vs temperature in Fig. 4a. At high temperatures ($T > 180$ mK) the transition is indicated by a change in slope in $T_s(H)$ (see the inset to Fig. 3), which is consistent with a second order transition and previous critical behavior analysis of the boundary at higher temperatures [3]. At lower temperatures ($80 \lesssim T < 180$ mK) we observe that $T_s(H)$ displays nonmonotonic behavior, with a drop of magnitude ΔT at H_c (see inset to Fig. 3). We see an equivalent rise in $T_s(H)$ on decreasing the field, and we associate the feature with a latent heat at the transition, implying that the transition is first order at the lowest temperatures. We plot the heat associated with ΔT, $C\Delta T$, at the transition field (H_c) in Fig. 4b.

We observe that, below $T_{\mathrm{min}} \sim 180$ mK, H_c increases as temperature decreases, thus demonstrating that the phase boundary does indeed have a minimum. We find that the phase boundary taken from $T_s(H)$ is in quantitative agreement with the previous estimate [3] and with our heat capacity data, and, except for the lowest temperatures, we find excellent agreement between data taken on raising and lowering the field, which implies that the existence of a minimum is not due to nonequilibrium effects. The slope of the low temperature phase boundary, and therefore the existence of a minimum, is confirmed by the Clausius-Clapeyron equation, since the sign of the latent heat implies dH/dT is negative along the phase boundary. The sign

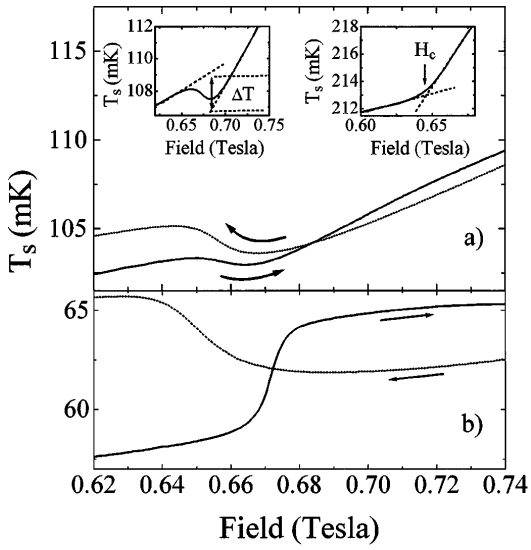

FIG. 3. The sample temperature, T_s, during field sweeps across the boundary between the IF and AFM phases. (a) At ~100 mK where the system shows a latent heat being absorbed and released at H_c during raising and lowering the field, respectively. (b) At ~60 mK where the system enters a metastable state before the transition is nucleated so that heat is released on either raising or lowering the field. The insets show how $T_s(H)$ changes near H_c at ~100 mK (left) where the transition is first order and at ~200 mK (right) where the transition is second order.

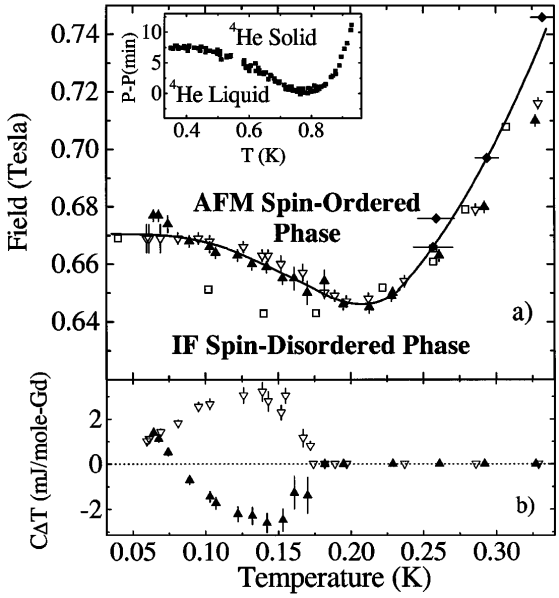

FIG. 4. (a) The phase boundary between the AFM and IF phases in the low and intermediate field regime. The solid diamonds are our $C(T)$ data. The open squares are the previous χ_{ac} data [3]. The up and down solid triangles are the $T_s(H)$ data for increasing and decreasing field, respectively, and the solid line is to guide the eye. The inset shows the melting curve of ^{4}He [19] for comparison. (b) The temperature change (ΔT) at the IF/AFM transition multiplied by the heat capacity, $C(T)$.

of the latent heat also implies that the change of entropy is positive going from the IF state to the AFM state. Note that $C\Delta T \rightarrow 0$ near the minimum in the phase boundary as expected from the Clausius-Clapeyron equation, and $C\Delta T = 0$ for $T \geq 0.18$ K corresponding to the transition becoming second order.

As shown in Fig. 3b, the increasing field data of $T_s(H)$ for $T < 80$ mK are qualitatively different from those taken at higher temperatures, showing heat release rather than absorption associated with the transition. This can be understood as a nonequilibrium effect associated with the first order nature of the transition [18]. For the sweeping up data, at the lowest temperatures, GGG remains in the metastable state (IF) even when the applied field is well above the equilibrium transition field. Eventually, the AFM state is nucleated and the energy difference with the metastable state results in a release of heat and a rise in $T_s(H)$. The nonequilibrium nature of the transition at the lowest temperatures is confirmed by a divergence between the increasing and decreasing field data for H_c below ~80 mK.

The minimum in the phase boundary of the AFM phase implies that the IF spin disordered phase is reentrant and has less entropy than the LRO AFM phase. The physical situation is quite different from that in "reentrant" spin glasses in which the spins go from a paramagnetic to a LRO phase to a spin glass phase on cooling [17]. In GGG the low temperature phase has *no* apparent spin ordering (not even spin glass order) and the low temperature state can be accessed without passing through an ordered phase (by cooling at a lower field). The reentrance of the IF state is more reminiscent of the minimum in the "melting" curve of ^{4}He, the phase line separating the solid and liquid phases (Fig. 4a inset). In the melting curve of ^{4}He [19] the minimum arises because the absence of transverse phonon modes in the liquid phase reduces the entropy of this phase to a value below that of the solid phase, which does have such modes. While no microscopic theory exists, one can easily imagine that there are more spin wave modes in the long range ordered AFM state of GGG than the spin disordered IF state. The boundary in GGG could then be viewed as being between a spin liquid in the IF phase and a long range ordered spin solid in the AFM phase.

We acknowledge the financial support of the NSF Grant No. DMR97-01548, ARO Grant No. DAAG55-98-1-0032, the Alfred P. Sloan Foundation, and the helpful discussions with G. Jones and D. A. Huse. We thank V. Fratello and A. J. Valentino at Bell Laboratories for sample preparation, and N. Kalechofsky (now at Oxford Instruments) for assistance in the early stages of these experiments.

[1] R. Liebmann, *Statistical Mechanics of Periodic Frustrated Ising Systems* (Springer-Verlag, Berlin, 1986); A. P. Ramirez, Annu. Rev. Mater. Sci. **24**, 453 (1994); R. Liebmann, *Magnetic Systems with Competing Interactions*, edited by H. T. Diep (World Scientific, Singapore, 1994); P. Schiffer and A. P. Ramirez, Comments Condens. Matter Phys. **18**, 21 (1996); M. J. Harris and M. P. Zinkin, Mod. Phys. Lett. B **10**, 417 (1996).

[2] M. J. P. Gingras *et al.*, Phys. Rev. Lett. **78**, 947 (1997); M. J. Harris *et al.*, Phys. Rev. Lett. **79**, 2554 (1997); B. D. Gaulin *et al.*, Physica (Amsterdam) **241B–243B**, 511 (1998).

[3] P. Schiffer *et al.*, Phys. Rev. Lett. **73**, 2500 (1994).

[4] O. A. Petrenko *et al.*, Physica (Amsterdam) **241B–243B**, 727 (1997); Phys. Rev. Lett. **80**, 4570 (1998).

[5] S. Hov, H. Bratsberg, and A. T. Skjeltorp, J. Magn. Magn. Mater. **15–18**, 455 (1980); S. Hov, Ph.D. thesis, University of Oslo, 1979 (unpublished).

[6] A. P. Ramirez and R. N. Kleiman, J. Appl. Phys. **69**, 5252 (1991).

[7] P. Schiffer *et al.*, Phys. Rev. Lett. **74**, 2379 (1995).

[8] A. P. Ramirez *et al.*, Phys. Rev. Lett. **64**, 2070 (1990); Phys. Rev. B **45**, 2505 (1992); Y. J. Uemura *et al.*, Phys. Rev. Lett. **73**, 3306 (1994); C. Broholm *et al.*, Phys. Rev. Lett. **65**, 3173 (1990).

[9] Details of the experiments and a complete data set are given elsewhere, Y. K. Tsui *et al.*, J. Appl. Phys. (to be published); Y. K. Tsui *et al.* (unpublished).

[10] W. I. Kinney and W. P. Wolf, J. Appl. Phys. **50**, 2115 (1979); W. I. Kinney, Ph.D. thesis, Yale University, 1979 (unpublished).

[11] W. P. Wolf *et al.*, J. Phys. Soc. Jpn. B1 **17**, 443 (1962); D. G. Onn, H. Meyer, and J. P. Remeika, Phys. Rev. **156**, 663 (1967); R. A. Fisher *et al.*, J. Chem. Phys. **59**, 4652 (1973).

[12] See, for example, R. Ballou, E. Lelièvre-Berna, and B. Fåk, Phys. Rev. Lett. **76**, 2125 (1996); R. Moessner and J. T. Chalker, Phys. Rev. Lett. **80**, 2929 (1998); B. Canals and C. Lacroix, Phys. Rev. Lett. **80**, 2933 (1998); M. J. Harris *et al.*, Phys. Rev. Lett. **81**, 4496 (1998); J. S. Gardner *et al.*, Phys. Rev. Lett. **82**, 1012 (1999), and references therein.

[13] B. Daudin, R. Lagnier, and B. Salce, J. Magn. Magn. Mater. **27**, 315 (1982).

[14] There are other systems in which spin excitations act as a scattering mechanism in phonon heat conduction, for example, G. S. Dixon, V. Benedict, and J. E. Rives, Phys. Rev. B **21**, 2865 (1980); C. Arzoumanian *et al.*, J. Phys. (Paris), Lett. **44**, L-39 (1983).

[15] Upon reexamination of the raw $\chi(H)$ data of Ref. [5], a small change in slope is observable at $H = 0.08$ T for $T = 0.38$ mK [P. Schiffer (unpublished)].

[16] G. J. Nieuwenhuys and J. A. Mydosh, Physica (Amsterdam) **86B–88B**, 880 (1977); A. Berton *et al.*, J. Phys. (Paris) **40**, L-391 (1979).

[17] K. H. Fischer and J. A. Hertz, *Spin Glasses* (Cambridge University Press, Cambridge, England, 1991).

[18] U. M. Scheven, E. I. Chashechkina, E. Lee, and P. M. Chaikin, Phys. Rev. B **52**, 3484 (1995).

[19] G. C. Straty and E. D. Adams, Phys. Rev. Lett. **17**, 290 (1966).