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Magnetic frustration and order in gadolinium gallium garnet

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Abstract

In gadolinium gallium garnet (GGG) there is no long-range magnetic order down to 25 mK even though the Curie–Weiss temperature is -2 K. Instead, over a wide temperature range GGG supports short-range magnetic order (spin liquid), while long-range order can be induced by an applied magnetic field. It is believed that the geometrical frustration of the magnetic interactions is responsible for this behaviour: in GGG the magnetic Gd ions are located on a *triangular* lattice. We have investigated the magnetic properties of GGG by neutron diffraction measurements. The results show clearly the development of short-range magnetic order without an applied field and the appearance of long range order in an applied magnetic field. A comparison of the experimental data with classical Monte Carlo simulations results provides us with firm conclusions about the relative strength of the magnetic interactions in GGG and their importance in the formation of a magnetic ground state.

Keywords: Spin liquid; Magnetic frustration; Monte Carlo simulation; Antiferromagnet

1. Introduction

Geometrical magnetic frustration prevents the formation of a single-ordered magnetic ground state but rather tends to create a magnetic system with a large number of possible ground states. In many ways this magnetic state is best described as a *spin-liquid*. Geometric frustration occurs when the magnetic atoms are positioned on an ordered lattice, but the system finds it impossible to satisfy the contradictory requirements for the orientation of the spin imposed by the interactions between the neighbouring spins. With dominant nearest-neighbour interactions such effects are typically found in two-dimensional corner and edge-sharing triangular nets, while in three dimensions corner and edge sharing tetrahedral arrangements of spins are also subject to strong frustrating influences.

Gadolinium gallium garnet, $Gd_3Ga_5O_{12}$ (GGG), occupies a unique position among the geometrically frustrated magnetic systems. It lies somewhere between the well-studied case of *stacked triangular* lattices [1] and lattices with a much more severe degree of frustration, such as the *Kagome-lattice* antiferromagnets [2] and the *pyrochlores* [3,4]. The former are magnetically ordered despite the frustration of the exchange interaction, the

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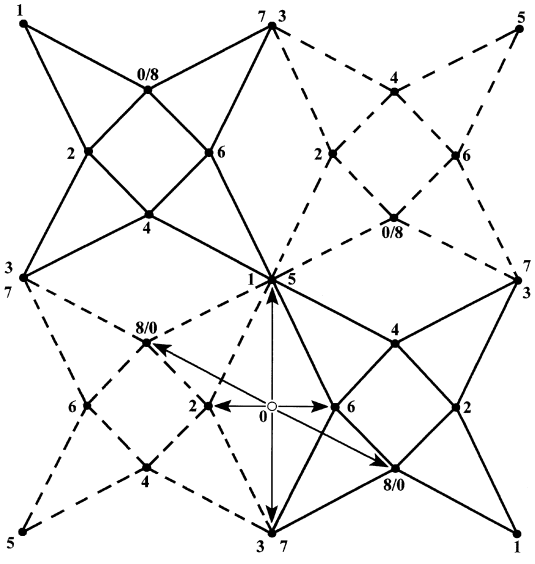

Fig. 1. Positions of the magnetic Gd ions in a garnet structure. The projection along a [0 0 1] direction is shown; numbers indicate heights, in units $a/8$, above the plane $z = 0$. There are 24 magnetic ions per unit cell, they are divided into two sublattices (solid and dashed lines). An open circle marks a Ga site, which could be occupied by an excess Gd ion; arrows indicate six nearest Gd ions for this site.

latter are not and are mostly spin-glasses at low temperatures. In GGG (space group $Ia\bar{3}d$) the magnetic Gd ions are located on two interpenetrating, corner-sharing triangular sublattices (Fig. 1). The triangles of spins do not lie in the same plane (the angle between two nearest triangles is equal to the angle between the diagonals of a cube, 73.2°), therefore the analogy with the *stacked triangular* lattice is not straightforward and an additional degree of freedom, which makes *Kagome* and *pyrochlores* lattices so magnetically different is still a possibility.

In GGG no sign of long-range magnetic order has been found down to 25 mK [5], moreover, frustration-induced spin freezing has been suggested at temperatures below 125–135 mK on the basis of single-crystal magnetisation measurements: the susceptibility is frequency dependent, and the static magnetisation is different for field cooling and zero-field cooling [6]. However, as we shall see neutron scattering experiments show that at the lowest temperatures the magnetic system is not frozen completely. It rather behaves as a mixture of a spin-liquid state with a set of rigid magnetic pieces nucleated around impurity centers. There are also theoretical considerations, namely mean-field calculations, which suggest that GGG shares no similarities with the *pyrochlore* or *Kagome* lattices since the dipolar forces lift the degeneracy of the ground state – at some low temperature there should be a phase transition to an incommensurate long-range-ordered (LRO) phase [7].

In the currently measured temperature range LRO can be induced only by an applied magnetic field of around 1 T, which results in a unique phase diagram for GGG [8,9]. On the other hand, similar gallium garnets based on Dy, Nd, Sm and Er, rather than Gd, have been found to be magnetically ordered at temperatures below 1 K [10,11]. It is very likely that the magnetic isotropy of GGG is responsible for such a striking difference: in a sharp contrast with the rest of rare-earth garnets single-ion anisotropy in GGG is almost zero and apart from the dipole–dipole anisotropy GGG is a perfect Heisenberg AFM.

In this paper we report the results of neutron diffraction measurements as well as classical Monte Carlo (MC) simulations of the magnetic properties of GGG. The necessity of the neutron scattering investigation of GGG was made evident by the predictions of susceptibility and heat capacity measurements: information about the microscopic magnetic correlations is crucial for an understanding of the magnetic properties. In addition, Monte Carlo simulations allowed us to check the importance of different magnetic interactions on the formation of the ground state. We concentrate mostly on a comparison of the simulation results with neutron scattering data, both in magnetic field and without field, although some other quantities, such as specific heat, magnetisation and susceptibility, have also been calculated. The results show good agreement with the experimental neutron diffraction data, as well as with previous bulk property measurements.

This paper is organized in the following way. The next section describes the details of the experimental procedure and computer simulation, a further section describes the results obtained, while the last section attempts to draw some conclusions.

2. Experimental details and sample preparation

GGG powder has been prepared from a stoichiometric mixture of Gd_2O_3 and Ga_2O_3 by a solid diffusion reaction at $T = 1400°C$ for 12 h. Natural Gd contains the isotope ^{157}Gd, which makes neutron scattering experiments impossible due to its very high absorption cross section. Therefore, we have prepared a sample with 99.98% of non-absorbing isotope, ^{160}Gd. This isotope was supplied by Oak Ridge National Laboratory.

The neutron scattering measurements in a zero magnetic field were carried out in the temperature range 40 mK–20 K using the instrument D1B at the Institute Laue-Langevin in Grenoble. The neutron wavelength was fixed at 2.52 Å, which allowed us to cover a momentum transfer range $Q = 0.2$–3.3 $Å^{-1}$ using a 80°-multidetector. Typical counting times for a 1.5 cm^3 sample were 2 h at each temperature. For the measurements in an applied magnetic field initial measurements were made using a triple axis spectrometer at ORNL. More extensive measurements were performed using a flat-cone diffractometer E2 (Berlin Neutron Scattering Center, Hahn-Meitner-Institut) with a multidetector covering an 80° scattering angle. A fixed, incident neutron wavelength at 2.4 Å was used for these measurements. An external magnetic field of up to 5 T was provided by a vertical split-pair cryomagnet. Significantly lower neutron flux was partially compensated by the longer counting times (typically 6 h at each temperature and field) and partially by the fact that the intensity of the magnetic Bragg reflections appearing in a field is much higher than the intensity of the broad magnetic diffuse peaks of the disordered state.

In these experiments the combination of a standard orange cryostat or an Oxford Instruments cryomagnet with a dilution refrigerator insert has provided sub-Kelvin temperatures. A copper sample holder filled with ^3He gas has been used instead of the usual aluminium can in order to secure better heat exchange at low temperatures.

3. Computer simulation models

Two attempts to simulate the magnetic properties of GGG (specific heat and ground state configuration in magnetic field) using the MC method had been made previously [9,12]. It is believed that the amplitudes of the nearest and next to nearest-neighbour interactions (up to a third neighbour) are well known from an early study by Kinney and Wolf [12]. In that paper three parameters (J_1, J_2 and J_3) have been determined from the comparison of the MC results with the temperature dependence of the specific heat. We use the same value of the nearest exchange constant, $J_1 = 0.107$ K, because it agrees well with the susceptibility temperature dependence and also with the saturation field for the magnetisation [13]. However, the well-known slowing down of the spin relaxation process due to the presence of dipole–dipole interactions, as well as the small number of MC steps per spin and relatively small size of the model raise a question mark against the previous results for J_2 and J_3. No such obvious questions as the minimum simulation time required to reach thermal equilibrium, the influence of the dipole–dipole cut-off range and size-dependence were considered in this previous work. Moreover, these probably inaccurate parameters, have been used for the calculation of the magnetic phase boundary [9], which turned out to be 30% outside the experimental boundary in both temperature and magnetic field.

Our MC simulations have been performed for lattice sizes $L \times L \times L$, where $L = 3$, 4 and 5 unit cells, containing 648, 1536 and 3000 spins, respectively. Significantly larger, than previously used, lattice sizes have ensured that the lattice size exceeds the magnetic correlation length in the spin-liquid phase and also have improved the resolution of the calculated neutron scattering function, $S(Q)$, in magnetic field allowing us to resolve clearly individual magnetic peaks associated with the LRO.

A standard Metropolis algorithm with periodic or open boundary condition has been employed; an attenuation factor δS has been introduced in such a way that roughly 50% of the attempted spin moves were accepted [14]. Despite the fact that the introduction of an attenuation factor has increased the spin relaxation rate dramatically, this procedure has been abandoned for the simulations in magnetic field in order to permit the system to make abrupt structure changes. Magnetic fields

have been applied along the three different directions: (1 1 1), (1 1 0) and (0 0 1), with emphasis on the (0 0 1) direction. In the low-temperature low-field region reliable information could be obtained only after a relatively long time, therefore up to a million Monte Carlo steps per spin (MCS) were performed at the lowest temperatures.

4. Results and discussion

4.1. Zero external field properties

The temperature evolution of the magnetic neutron scattering pattern is shown in Fig. 2. The magnetic data were obtained from the raw data by subtracting the higher-temperature background signal. In the temperature range 1.3–5 K the scattering pattern is similar to the structure factor of a classical fluid of hard spheres [15]. The two very broad diffuse scattering peaks at 1.05 and 2.87 Å^{-1} are due to antiferromagnetic exchange interaction between nearest neighbour Gd magnetic moments. The intensity of both these peaks increases as the temperature decreases. At temperatures around and below 1 K a third broad peak is observed at $Q = 1.7$–$1.8\,\text{Å}^{-1}$. A deviation from a symmetric Gaussian shape was seen when the temperature has lowered below 0.5 K: the strongest peak becoming more and more asymmetric, and finally, at $T <$ 140 mK a new set of much sharper peaks appeared on top of the broad peaks. This temperature, at which the "sharp" peaks appear, is the same as the "spin freezing" temperature, as estimated from single crystal magnetisation and specific heat measurements [6].

About 10 new magnetic peaks are visible at the lowest temperature. Their positions could not be described with integer or half-integer nuclear indexes ($h\,k\,l$), most likely they are incommensurate with the nuclear structure. With a further decrease in temperature the intensity of these new "sharp" peaks increases, while the intensity of broad diffuse scattering peaks is slightly decreased. The temperature dependence of the intensity of the "sharp" peaks indicates a continuous build up of the magnetic correlations below 140 mK and a partial redistribution from the "liquid" phase to a "solid" phase, rather than freezing. From the temperature dependence of the integrated intensity of the diffuse scattering peaks a coarse estimation may be made that even at the lowest temperature about 85% of the volume remains in the liquid phase.

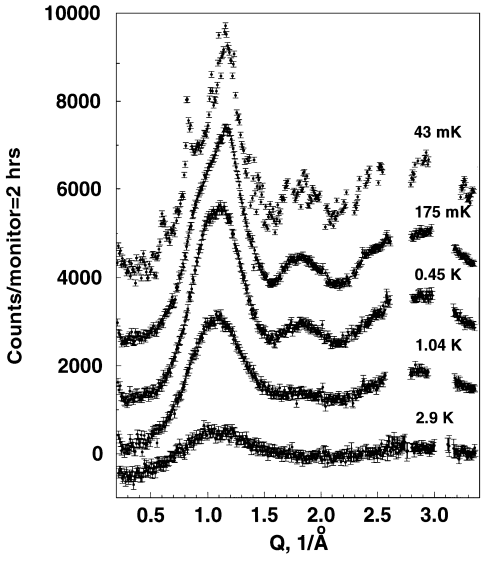

Fig. 2. Low-temperature neutron-diffraction data, $I(Q)$, for gadolinium gallium garnet after subtracting the 9 K data. The curves for different temperatures are separated for clarity.

The width of the "sharp" peaks decreases only slightly with decreasing temperature and even at lowest temperature these peaks are about twice as broad as would be expected given the diffractometer's resolution, which suggests the absence of true long-range magnetic ordering. The correlation length of the ordered magnetic regions is approximately 100 Å.

MC simulations for the model, which includes only nearest-neighbour exchange, J_1, do not show any sign of a phase transition down to at least $T = 5$ mK. The system remains in a spin-liquid phase: averaging over a sufficiently long time gives zero magnetic moment on each site, there is no maximum or cusp in the calculated heat capacity and the estimated scattering function, $S(Q)$, matches perfectly the experimental data at all temperatures for $T > 140$ mK and demonstrates only broad diffuse scattering peaks. However, we restrain ourselves from a discussion as to whether or

not this system will order at some lower temperature or only at $T = 0$. Instead, we simply claim that the system is not ordered down to at least $T = 0.004\,JS^2$.

The introduction of a dipole–dipole interaction slows down the spin-relaxation process. For instance, in the model, which includes dipole–dipole interactions, the autocorrelation function, $1/N\sum_i^N \langle S_i(0)S_i(t)\rangle$ does not show visible relaxation and remains almost equal to unity at and below $T = 50\,\mathrm{mK}$, while in the model with only nearest exchange interactions it is still relaxing towards zero even at $T = 5\,\mathrm{mK}$. The difference between the two models is evident at all temperatures below 0.5 K, which approximately coincides with the nearest neighbour dipole energy.

An interesting question to investigate is how the ratio of exchange to dipolar interactions influences the magnetic properties of GGG. In GGG the nearest-neighbour exchange, J_1, is about twice the strength of the nearest-neighbour dipolar interactions, *DD*, and there is no magnetic order, while in the very similar magnetically isotropic garnets $Mn_3Al_2Ge_3O_{12}$ and $Mn_3Al_2Si_3O_{12}$ [16] the ratio J_1/DD is slightly higher and they do order. For instance, in $Mn_3Al_2Ge_3O_{12}$, which undergoes an antiferromagnetic phase transition to a 120°-structure at $T_N = 6.65\,\mathrm{K}$, the $J_1 = 0.57\,\mathrm{K}$ [17] is more than ten times stronger that *DD*. Could this fact alone lead to the appearance of long-range magnetic order? Our simulation results does not seem to support this idea: in a model, where J_1 has been increased up to a hundred times keeping the *DD* value fixed, the ground state remained disordered. However, the introduction of a next-to-nearest exchange interaction with a value cited in Ref. [16], $J_2 = 0.12\,\mathrm{K}$, does make a difference: the system immediately undergoes a phase transition to a LRO state.

What is the origin of the sharp peaks? We suggest it is due to a minor chemical disorder in $Gd_3Ga_5O_{12}$ samples. In GGG there is a tendency for the Gd ions to occupy Ga sites (see Fig. 1), which may results in a 0.3–1.0% excess of Gd above the stoichiometric composition. The low-temperature spin-glass transition has found to be sample dependent [6], therefore the influence of impurities or chemical disorder could not be ruled out.

To test this possibility we have performed MC simulations on a GGG model with one additional Gd ion occupying a Ga site (which corresponds to less than 0.1% Gd excess for our system). The excess Gd ion is slightly closer to the six nearest neighbours than the ordinary Gd ions, therefore it should interact more strongly with the neighbours. The results of the simulations show, that even if $J_{\mathrm{imp}} = J_1$, magnetic order occurs around the impurity ion at sufficiently low temperature. The magnetic correlation length becomes compatible with the size of the model. In fact, the introduction of an additional Gd ion, instead of Ga, results in an increase of the intersublattice interaction, therefore the increase of the correlation length is quite predictable.

4.2. Magnetic properties in an applied field

The application of an external magnetic field causes a dramatic change in the neutron scattering pattern. Two sets of magnetic Bragg peaks, ferromagnetic and antiferromagnetic, appear in a field instead of broad diffuse scattering peaks. The former have intensity increasing with the field and saturate at some high field (above 3.5 T), the latter have intensity growing in low fields, reaching a maximum at $H = 1\,\mathrm{T}$, then decreasing and disappearing at a field above 2 T. Fig. 3 shows an evolution of the neutron scattering diffraction pattern with an applied magnetic field. As it can be seen from the figure, the very broad peaks, corresponding to the short-range magnetic order (spin-liquid), gradually disappear in an applied field. The intensity of the majority of nuclear peaks is greatly increased in a field due to the ferromagnetic contribution even at relatively high temperature (above 1 K). The strongest antiferromagnetic peaks, such as (2 0 0), (2 1 0) and the incommensurate peak located between them, are clearly visible in a magnetic field below 2 T. Quite clearly the magnetic structure in a field differs from 120° configuration observed in similar magnetically isotropic garnets $Mn_3Al_2Ge_3O_{12}$ and $Mn_3Al_2Si_3O_{12}$ [16].

The results of the neutron scattering experiments agree qualitatively with the bulk properties measurements, however, the actual phase diagram of GGG seems to be more complicated: long-range

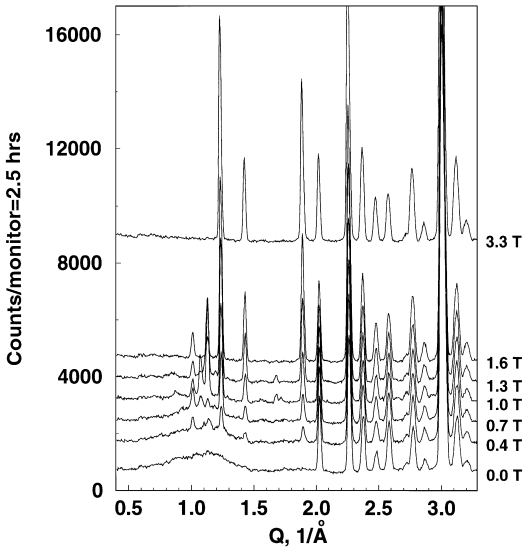

Fig. 3. Neutron diffraction pattern of GGG at $T = 180\,\mathrm{mK}$ in applied magnetic field. The curves for different fields are separated by $2500 \times H$ counts for clarity.

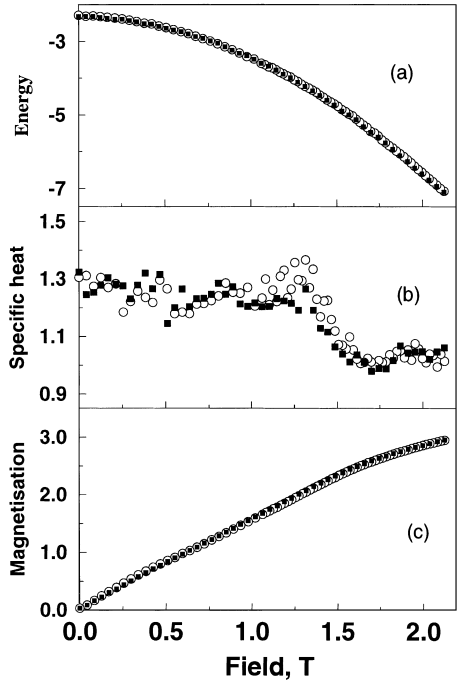

Fig. 4. MC field dependence at $T = 0.2\,\mathrm{K}$ of the total energy (a), specific heat (b) and magnetisation (c) per spin for a $3 \times 3 \times 3$ model which includes J_1 and the dipolar interactions (open symbols) and for a model which includes J_2 and J_3 as well (solid symbols).

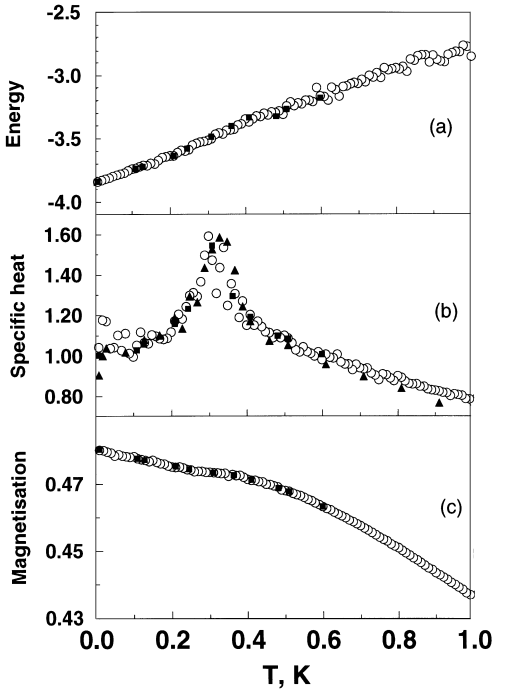

Fig. 5. MC temperature dependence at $H = 1.06\,\mathrm{K}$ of the system energy (a), specific heat (b) and magnetisation (c) per spin for a $3 \times 3 \times 3$ model which includes J_1 and dipole–dipole interaction. 10^5 (open circles) and 10^6 (solid squares) MCS have been performed. For comparison purposes the triangular on part (b) represent the results of a specific heat calculations for a $4 \times 4 \times 4$ model.

magnetic order has been induced by a field around 0.4 T, while the bulk properties measurements showed LRO only above 0.7 T. In addition, each of the antiferromagnetic peaks vanishes at different values for the applied magnetic field. Unfortunately, the experimental difficulties did not allow us to cool the sample below 140 mK, where there is a partial transition to a phase with a much longer correlation length.

In an applied magnetic field the problem of long equilibration times is much less severe, which provides us with an opportunity to investigate the magnetic phase diagram of GGG in detail. Phase transitions to a LRO state in an applied magnetic field could be detected, for example, by calculating the specific heat temperature dependence in constant field or by calculating its field dependence at constant temperature. In order to avoid problems

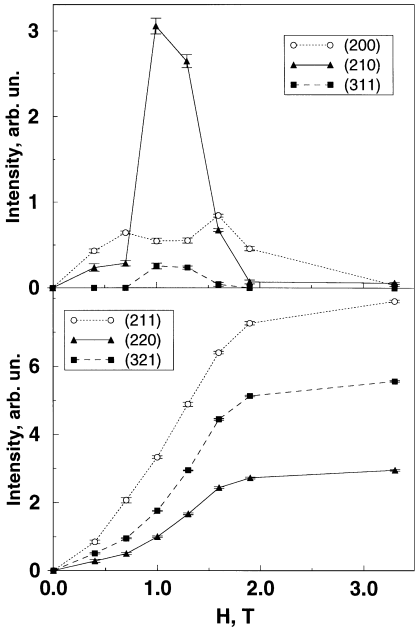

Fig. 6. Field dependence of the intensities of the antiferromagnetic (top) and ferromagnetic (bottom) neutron scattering peaks of GGG at $T = 180\,\mathrm{mK}$.

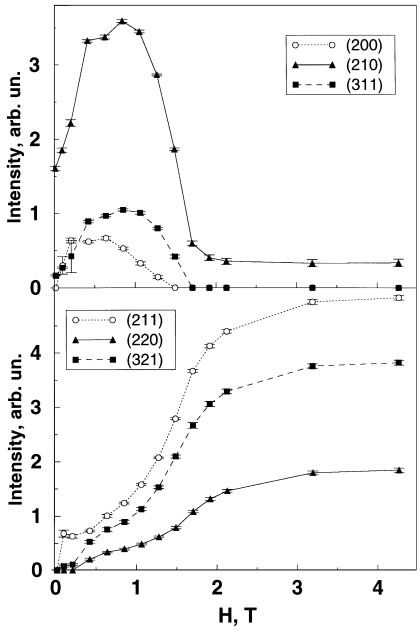

Fig. 7. Field dependence of the intensity of neutron scattering peaks obtained from the MC simulations.

with possibly many metastable states the calculations were always started at high temperatures and fields and then the system annealed as it came into equilibrium at the desired field and temperature for measurement. Figs. 4 and 5 present examples of such experiments. Several conclusions can be drawn from these results. Firstly, the position of the phase transition in the $T - H$ coordinates is not sensitive to the introduction of the next-to-nearest exchange interactions with the values quoted in [12], $J_2 = -0.003\,\mathrm{K}$ and $J_3 = 0.010\,\mathrm{K}$, neither does it show any size dependence. Secondly, in the field dependence of the specific heat, only one anomaly corresponding to the upper transition field is clearly seen, while there is no obvious anomaly corresponding to the lower transition field, which agrees with previous MC simulations [9].

Although calculation of the neutron scattering function, S(Q), as a $\sum_{i,j}\langle \mathbf{S}_i\mathbf{S}_j\rangle \sin(Qr)/(Qr)$ is not valid with long-range magnetic order (the positions of the Bragg peaks is still correct, but their intensity is not) the field dependence of these peaks demonstrates a remarkable similarity with the experimental data. Figs. 6 and 7 show the experimental and simulated field dependence of the magnetic Bragg peaks, respectively.

It should be especially emphasised, that no antiferromagnetic peaks have been observed in any model, which excludes the dipolar forces.

5. Conclusions

In conclusion, we have investigated the low temperature behaviour of the frustrated triangular antiferromagnet, $Gd_3Ga_5O_{12}$, by neutron diffraction measurements and classical Monte Carlo simulations. Both a spin-liquid phase, arising from the nearest neighbour exchange interaction, and a unique mixed liquid–solid state, most likely caused by minor chemical disorder, has been observed. In an applied magnetic field long-range-ordered incommensurate magnetic structure appeared around $H = 1\,\mathrm{T}$.

From a magnetic point of view what we see in GGG is just a consequence of a very rare

conjunction of the magnetic parameters rather than inherent property of the geometrically frustrated lattice. The requirements for an antiferromagnet on a similar lattice to behave as GGG does are:

- Complete exchange isotropy, the single-ion anisotropy should be almost zero. What happens if there is a preferred orientation for the spins is quite obvious both from the simulations and from the experiments in magnetic field: LRO occurs almost simultaneously with the application of the magnetic field.
- J_1 is by far the strongest magnetic exchange interaction in a system. Sufficiently strong intersublattice interaction, J_2, forces the system to order. Some combinations of the relatively small J_2–J_4 interactions may also produce long-range magnetic order.
- A sufficiently strong dipole–dipole interaction is required.
- A low level of chemical disorder is necessary.

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