Investigation of the Low-Temperature Spin-Liquid Behavior of the Frustrated Magnet Gadolinium Gallium Garnet

O. A. Petrenko,[1] C. Ritter,[2] M. Yethiraj,[3] and D. McK Paul[1]
[1]*Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom*
[2]*Institut Laue-Langevin, 156X, 38042 Grenoble Cedex, France*
[3]*Solid State Division, ORNL, Oak Ridge, Tennessee 37831-6393*
(Received 7 July 1997)

We report the results of powder neutron scattering measurements on the magnetic correlations in the frustrated antiferromagnet $Gd_3Ga_5O_{12}$. A clear view of the short-range magnetic order has been obtained for a temperature range 0.14–5 K. At $T \sim 0.14$ K there is a partial transition to a phase with a much longer correlation length. We argue that the low-temperature phase is not an ordinary spin glass, as was suggested by bulk properties measurements, but rather a mixture of a spin-liquid state with a set of rigid magnetic pieces nucleated around impurity centers. The experimental data are compared with the results of Monte Carlo simulations performed for several models. [S0031-9007(98)06071-2]

PACS numbers: 75.25.+z, 75.40.Mg, 75.50.Ee, 75.50.Lk

The effect of frustration on the magnetic properties of a variety of magnetic systems has been intensively discussed in the last decade. In magnetic systems, without nuclear disorder, frustration is caused by competition between nearest neighbor exchange interactions or between nearest and next nearest neighbor interactions. One of the most evident examples of the former case (so-called geometric frustration) is an antiferromagnet on a triangular lattice. There are several ways in which triangles of antiferromagnetic interactions can be built into a crystal lattice, among these *stacked triangular* lattices, *Kagome*-lattices, and lattices of corner-sharing tetrahedra have attracted both theoretical and experimental attention. The distinguishing feature of the majority of antiferromagnets on a *stacked triangular lattice*, containing two-dimensional triangular sheets, is the appearance, at sufficiently low temperature, of three-dimensional long-range magnetic ordering, despite the frustration of the exchange interaction [1]. The influence of frustration on the magnetic properties of other triangular antiferromagnets (with more complicated geometry) is apparently more substantial. For example, in the Kagome-lattice antiferromagnet $SrCr_{9p}Ga_{12-9p}O_{19}$, with $p \approx 0.9$ [2], the low-temperature ground state is a spin glass. Many *pyrochlores* with the chemical formula $A_2B_2O_7$, where the spins are located on two interpenetrating lattices of corner-sharing tetrahedra, also undergo a phase transition to a spin glass state [3,4].

In this Letter we report the first neutron scattering measurements on a powder sample of gadolinium gallium garnet, $Gd_3Ga_5O_{12}$ (GGG), where the magnetic Gd ions are located on two interpenetrating corner-sharing triangular sublattices (Fig. 1). 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 a temperature below 125–135 mK on the basis of single crystal magnetization measurements: the susceptibility is frequency dependent, and the static magnetization is different for field cooling and zero field cooling [6]. However, the neutron scattering experiments on a polycrystalline sample show that at the lowest temperatures the magnetic system is not frozen completely.

Long-range magnetic order in GGG has been found only in an applied magnetic field around 1 T [7,8]. On the other hand, similar gallium garnets of Dy, Nd, Sm, and Er have been found to be magnetically ordered at temperatures below 1 K [9]. What causes such a different degree of frustration? Which interactions play a crucial role in forming short- and long-range magnetic order? In this Letter we intend to answer, at least partially, these fundamental questions.

Direct microscopic information about the spin configuration can be obtained from neutron diffraction studies. The necessity of such an investigation of GGG has

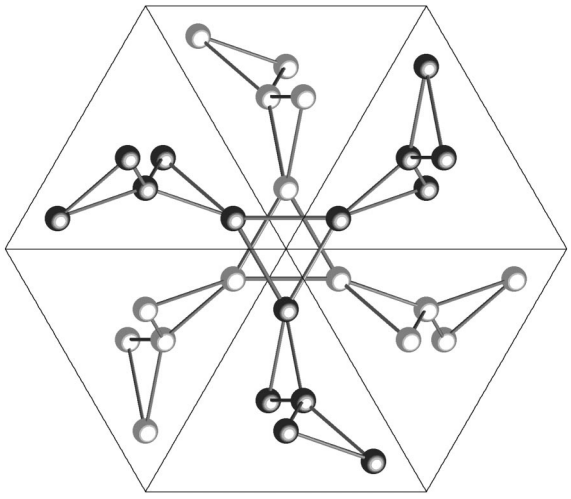

FIG. 1. Positions of the magnetic Gd ions in a garnet structure. The projection along a [111] direction is shown. There are 24 magnetic ions per unit cell, they are divided into two interpenetrating sublattices.

 0031-9007/98/80(20)/4570(4)$15.00

become evident from the results of susceptibility and heat capacity measurements. However, natural Gd contains isotope ^{157}Gd, which makes neutron scattering experiments impossible due to a very high absorption cross section ($\sigma \approx 254\,000$ barns for $\lambda = 1.8$ Å). Therefore, we have prepared a sample with 99.98% of nonabsorbing isotope, ^{160}Gd, ($\sigma \approx 0.77$ barns) supplied by the Oak Ridge National Laboratory.

GGG powder has been prepared from a stoichiometric mixture of Gd_2O_3 and Ga_2O_3 by a solid diffusion reaction at $T = 1400\,^{\circ}$C for 12 hours with intermediate regrinding. The procedure of regrinding was repeated until an x-ray diffraction study did not reveal any impurity phases in the final product. The neutron scattering measurements were carried out in the temperature range 40 mK–20 K using the instrument D1B at ILL, Grenoble. (002) reflections from three focusing pyrolytic graphite crystals were used to monochromatize the neutron beam; 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 an 80° multidetector [$Q = 4\pi \sin(\theta)/\lambda$]. Typical counting times for a 1.5 cm^3 sample were 2 h at each temperature. A copper sample holder filled with ^{3}He gas has been used instead of the usual aluminum can in order to provide better heat exchange at low temperatures.

The temperature evolution of the magnetic neutron scattering pattern is shown in Fig. 2(a). The magnetic data were obtained by subtracting the nuclear intensity measured at $T = 9$ K. In the higher temperature range (1.3–5 K) the scattering pattern looks similar to the structure factor of a classical fluid of hard spheres [10]. The two very broad diffuse scattering peaks at 1.05 and 2.87 Å^{-1} are due to antiferromagnetic exchange interaction between nearest neighbor Gd magnetic moments separated by the distance $(\sqrt{6}/8)a = 3.781$ Å (the lattice constant at low temperature was found to be $a = 12.349$ Å). 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 Å^{-1}. A deviation from a symmetric Gaussian shape was seen when the temperature was 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, suggested on the basis of single crystal magnetization and specific heat measurements [6].

About ten new peaks are clearly visible at the lowest temperature [see Fig. 2(b)]. Their positions could not be described with integer or half integer nuclear indexes (hkl); most likely they are incommensurate with the nuclear structure. Quite clearly the magnetic structure in the low-temperature phase differs from 120° configuration observed in similar magnetically isotropic garnets $Mn_3Al_2Ge_3O_{12}$ and $Mn_3Al_2Si_3O_{12}$ [11]. With a further

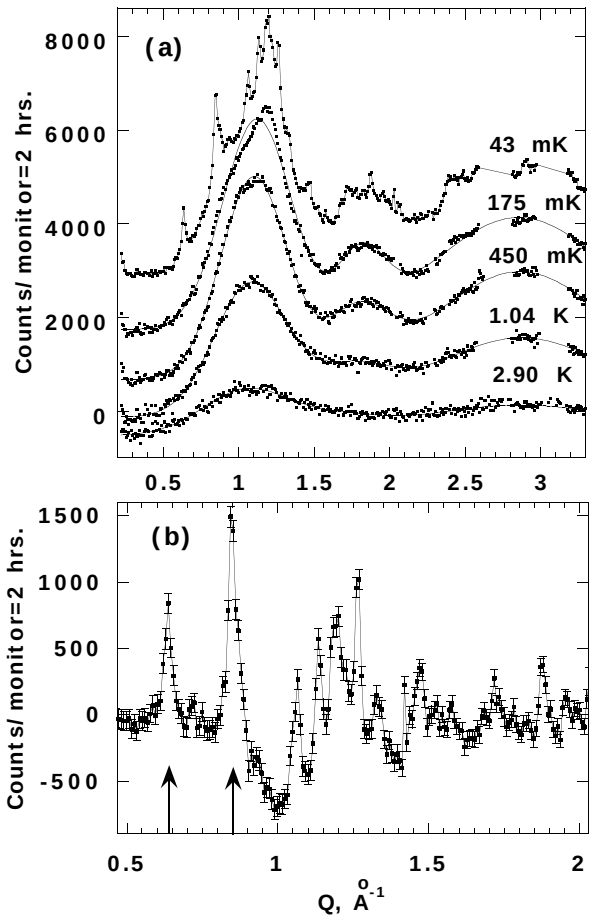

FIG. 2. (a) Low-temperature neutron diffraction data, $I(Q)$, for gadolinium gallium garnet after subtracting the 9 K data. The curves for different temperatures are separated by 1200 counts for clarity. The intensity has been fitted with three Gaussian functions (solid lines) in order to determine position, intensity, and width of the broad diffuse scattering peaks. (b) Difference plot for temperatures 43 and 175 mK underlining the appearance of the sharp magnetic peaks. Arrows indicate the position of two magnetic peaks, whose intensities are shown in Fig. 3.

decrease in temperature the intensity of these new sharp peaks is increased, while the intensity of broad diffuse scattering peaks is slightly decreased. Figure 3 presents the temperature dependence of the intensity of the two strongest sharp peaks, indicating a continuous build up of the magnetic correlations below 140 mK and redistribution from a "liquid" phase to a "solid" phase, rather than freezing. From the temperature dependence of the integrated intensity of the main broad diffuse scattering peak at $Q = 1.05$ Å^{-1}, the coarse estimation could be given that at the lowest temperature $T = 43$ mK about 85% of the volume remains in a liquid phase.

The width of the sharp peaks decreases only slightly with temperature decrease and even at the lowest temperature these peaks are about twice as broad as those expected given the diffractometer's resolution, which suggests the absence of true long-range magnetic ordering.

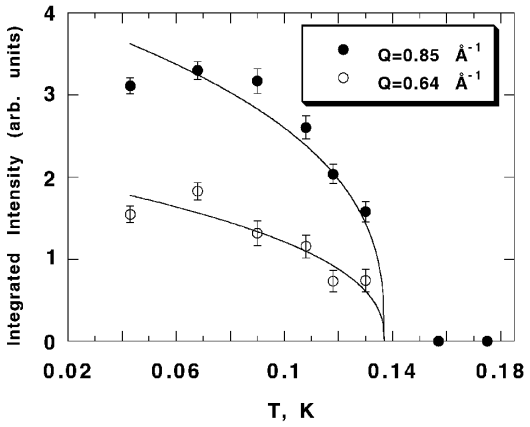

FIG. 3. Temperature dependence of the integrated intensity of the two strongest magnetic peaks at $Q = 0.64$ Å^{-1} (open symbols) and $Q = 0.85$ Å^{-1} (closed symbols). Solid lines are guides for the eye.

The correlation length of the magnetic interaction is approximately 100 Å.

A somewhat better insight into the short-range correlation can be obtained by Fourier transforming the data, $I(Q)$, which gives the radial correlation function, $G(r)$. Figure 4 shows a set of correlation functions at different temperatures, where arrows indicate the positions of the eight nearest neighbors for Gd ions. The most important conclusion to be drawn from this figure is that with the decrease of temperature, the correlations mostly build up inside of the sublattices, while the intersublattice interaction remains relatively weak, thus confirming the fact that nearest neighbor antiferromagnetic exchange is dominant over the other magnetic forces.

In order to understand the importance of the different interactions on the formation of magnetic order, we have performed Monte Carlo (MC) simulations and calculated the bulk properties and neutron scattering function $S(Q)$ of GGG. We use the same value of the exchange constant, $J_1 = 0.107$ K, as in previous MC simulations [8,12], but extend dipole-dipole interaction up to a fourth neighbor and also use significantly bigger lattice sizes (up to $5 \times 5 \times 5$ unit cells). A standard Metropolis algorithm with periodic or open boundary conditions has been employed; an attenuation factor δS has been introduced in such a way that roughly 50% of the attempted spin moves were accepted [13], up to a million Monte Carlo steps per spin (MCS) were performed at the lowest temperatures. The results of the simulations can be summarized as follows:

(1) The neutron scattering function $S(Q)$ at temperatures well above 140 mK with two and three broad diffuse scattering peaks could be described taking into account only the nearest neighbor exchange interaction, J_1. The introduction of the dipole-dipole interaction and next to nearest exchange interactions at these temperatures does not change $S(Q)$ significantly, it rather influences the specific heat in the sense that it produces a broad peak at temperature below 1 K in agreement with the experimental observations [6,12]. Figure 5 gives some examples of the simulated $S(Q)$ at different temperatures.

(2) In a model which includes only J_1 there is neither long-range ordering nor a spin glasslike metastable state down to at least $T = 1$ mK. The magnetic correlation length does not exceed the unit cell size at any temperature. In agreement with previous MC simulations, the introduction of the dipole-dipole interaction causes a dramatic slowing down of the relaxation processes.

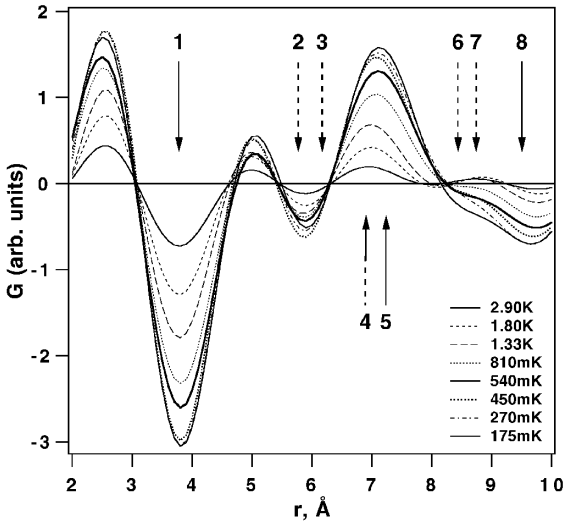

FIG. 4. Radial correlation function $G(r)$ at different temperatures. The data were obtained by Fourier transformation of the difference data sets, $I(Q)$, after numerical smoothing. The arrows indicate eight nearest neighbor distances for Gd-Gd bonds: solid arrows correspond to intrasublattice bonds; dashed arrows mark intersublattice bonds.

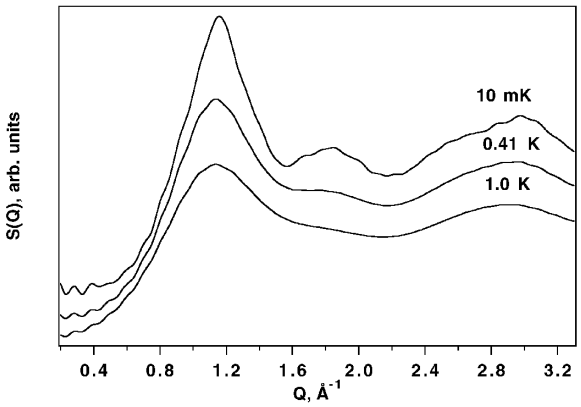

FIG. 5. The examples of the Monte Carlo simulated neutron scattering function $S(Q)$ at different temperatures; the model includes nearest neighbor exchange interaction only, model size is $5 \times 5 \times 5$ unit cells; 10^5 MCS were performed for each temperature.

(3) The neutron scattering function is not sensitive to a small change ($\pm 20\%$) of J_1 if the dipole-dipole interactions remains the same, but it is very sensitive to some combinations of J_2, J_3, and J_4. For example, in the case of a small antiferromagnetic intersublattice interaction ($J_2 = 0.01$ K), even a very small (less then 2% of J_1) ferromagnetic exchange with a next to nearest neighbor within the same sublattice, J_4, is enough to produce long-range magnetic order. These observations underline, once again, the fact that the ground state of the frustrated magnetic system is usually determined by a delicate balance of all the magnetic forces, including those which are relatively weak and could be completely ignored in nonfrustrated systems.

Although the results of the MC simulations with the model described so far fit our experimental data at higher temperature, a transition to the low-temperature state, where a spin-liquid coexists with another phase, requires further development of the model. In GGG there is a tendency for the Gd ions to occupy Ga sites, which results in the 0.3%–1.0% excess of Gd above the stoichiometric composition. The low-temperature transition was found to be sample dependent [6], therefore the influence of impurities or chemical disorder could not be ruled out. An analogy could be drawn here between the triangular antiferromagnet GGG and other examples of frustrated magnetic systems, such as a *XY* square-lattice antiferromagnet dominated by second-neighbor antiferromagnetic exchange and the spin-Peierls system $CuGeO_3$. In a first case dilution acts against thermal and quantum fluctuations, producing an effect known as "ordering due to disorder" [14]. In a second case an introduction of impurity ions (Zn or Ni) or the replacement of Ge ions with Si at the level of 1%–5% gives rise to the appearance of a new three dimensionally ordered magnetic phase [15].

We have performed MC simulations on a GGG model with one additional Gd ion occupying a Ga site (which corresponds to less then 0.1% Gd excess for our system). The excess Gd ion is slightly closer to the six nearest neighbors than the ordinary Gd ions, therefore it should strongly interact with the neighbors. The results of the simulations show that even if $J_{\mathrm{imp}} = J_1$, magnetic order occurs around an impurity ion at sufficiently low temperature. The magnetic correlation length becomes compatible with the size of the model. In fact, an 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. It would be very interesting to simulate a system with many impurities and a much bigger lattice size, where an interaction between magnetically ordered "islands" nucleated by the impurities could be studied.

In conclusion, we have investigated the low-temperature behavior of the frustrated triangular antiferromagnet, GGG, by the neutron diffraction measurements and classical Monte Carlo simulations. Both a spin-liquid phase, arising from the nearest neighbor exchange interaction, and a unique mixed liquid-solid state, most likely caused by minor chemical disorder, have been observed.

We thank J. N. Reimers and T. Harringan for their help with computer calculations. We also thank P. Schiffer and M. Zhitomirsky for the discussions of this problem. Work at the University of Warwick was supported by the EPSRC Grant *Correlated Magnetic Systems*, and the work at Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research Corporation under Contract No. DE-AC05-96OR22464.

[1] For a review article on stacked triangular antiferromagnets, see M. F. Collins and O. A. Petrenko, Can. J. Phys. **75**, 605 (1997).
[2] A. P. Ramirez, G. P. Espinosa, and A. S. Cooper, Phys. Rev. Lett. **64**, 2070 (1990).
[3] B. D. Gaulin, in *Magnetic Systems with Competing Interactions*, edited by H. T. Diep (World Scientific, Singapore, 1994), p. 286.
[4] M. J. P. Gingras, C. V. Stager, N. P. Raju, B. D. Gaulin, and J. E. Greedan, Phys. Rev. Lett. **78**, 947 (1997).
[5] A. P. Ramirez and R. N. Kleiman, J. Appl. Phys. **69**, 5252 (1991).
[6] P. Schiffer, A. P. Ramirez, D. A. Huse, P. L. Gammel, U. Yaron, D. J. Bishop, and A. J. Valentino, Phys. Rev. Lett. **74**, 2379 (1995).
[7] S. Hov, H. Bratsberg, and A. T. Skjeltorp, J. Magn. Magn. Mater. **15–18**, 455 (1980).
[8] P. Schiffer, A. P. Ramirez, D. A. Huse, and A. J. Valentino, Phys. Rev. Lett. **73**, 2500 (1994).
[9] J. Filippi, J. C. Lasjaunias, A. Ravex, F. Tcheou, and J. Rossat-Mignod, Solid State Commun. **23**, 613 (1977); D. G. Onn, H. Meyer, and J. P. Remeika, Phys. Rev. **156**, 663 (1967).
[10] N. W. Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966); N. W. Ashcroft, Physica (Utrecht) **35**, 148 (1967).
[11] W. Prandl, Phys. Status Solidi (b) **55**, K159 (1973).
[12] W. I. Kinney and W. P. Wolf, J. Appl. Phys. **50**, 2115 (1979).
[13] J. N. Reimers, Phys. Rev. B **45**, 7287 (1992).
[14] C. L. Henley, Phys. Rev. Lett. **62**, 2056 (1989).
[15] J.-G. Lussier, S. Coad, D. McMorrow, and D. McK Paul, J. Phys. Condens. Matter **7**, L325 (1995).