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Adiabatic demagnetization of a pyrochlore antiferromagnet $Gd_2Ti_2O_7$

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Abstract

An adiabatic demagnetization process is studied in the pyrochlore antiferromagnet $Gd_2Ti_2O_7$. A strong cooling of the sample is observed by decreasing magnetic field in the range 120–60 kOe corresponding to a crossover between saturated and spin–liquid phases. This phenomenon indicates that a considerable part of the magnetic entropy associated with a macroscopic number of local soft modes survives in the strongly correlated paramagnetic state. Monte Carlo simulations demonstrate good agreement with the experiment. The cooling power of the process is experimentally estimated with a view to possible technical applications. The results on $Gd_2Ti_2O_7$ are compared to those for $Gd_3Ga_5O_{12}$, a related material for low-temperature magnetic cooling.

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Nearest-neighbor antiferromagnets on typical geometrically frustrated structures, like, for instance, kagome, garnet, and pyrochlore lattices have an infinite number of classical ground states which precludes any type of conventional magnetic ordering. As a result, frustrated magnets remain in a disordered cooperative paramagnetic ground state at temperatures well below the paramagnetic Curie–Weiss constant [1]. A number of geometrically frustrated magnets have been experimentally studied in the past decade, among them is a Heisenberg pyrochlore compound $Gd_2Ti_2O_7$. Recent specific heat, susceptibility and neutron-scattering measurements [2–4] confirmed the existence of a wide temperature range between the Curie–Weiss constant $\Theta_{CW} \approx 10\,K$ and the temperature of an ordering transition. (The latter occurs only below 1 K presumably due to weak dipole–dipole interactions.) Infinite degeneracy of the magnetic ground state of a frustrated magnet is equivalent to presence of a macroscopic number of local zero-energy modes. Such soft modes correspond to degrees of freedom, which rotate a finite number of spins with no change in the total exchange energy. In a pyrochlore structure (a matrix of corner-sharing tetrahedra on the fcc lattice), these groups of spins are hexagons formed by the edges of neighboring tetrahedra, which lie in the kagome planes [1 1 1] and

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equivalent planes]. In zero field, if the six spins are arranged antiferromagnetically around one hexagon, they effectively decouple from the other spins and can rotate by an arbitrary angle. The low-energy hexagon modes have been observed in quasielastic neutron-scattering studies on spinel compound $ZnCr_2O_4$ [5], which is also a spin-3/2 Heisenberg antiferromagnet on a pyrochlore lattice. The thermodynamic consequence of these local excitations is that a considerable fraction of the magnetic entropy is not frozen down to temperatures much less than Θ_{CW}. This entropy can be eliminated by external magnetic field driving the system into a nondegenerate fully polarized spin state above H_{sat}. The enhanced magnetocaloric effect in strongly frustrated magnets recently explained in Ref. [6] and studied in the present work for a pyrochlore compound $Gd_2Ti_2O_7$ is the easiest physical probe of the frustrated ground state properties. The enhanced magnetic cooling power of gadolinium gallium garnet $Gd_3Ga_5O_{12}$ has been known for a long time [7], although without reference to frustrated properties of a garnet (hyper-kagome) lattice. As was predicted in Ref. [6], a stronger frustration on a pyrochlore lattice should produce the maximal cooling rate among geometrically frustrated magnets. Demagnetization of a $Gd_2Ti_2O_7$ sample under quasi-adiabatic conditions is measured and classical Monte Carlo (MC) simulations of an ideal adiabatic demagnetization process is performed. Entropy variations and the cooling power of $Gd_2Ti_2O_7$ are experimentally estimated.

A single-crystal $Gd_2Ti_2O_7$ sample of approximately $3.5 \times 1.5 \times 1\,mm^3$ in size (32.5 mg by mass) was grown by the method described in Ref. [8]. A commercially available RuO_2 thermometer with the resistance calibrated down to 100 mK in fields up to 120 kOe was glued onto the sample. It was also used as a heater to regulate the starting temperature of the experiment. The sample was suspended on four thin constantan wires (20 μm in diameter and 5 cm in length) soldered to the thermometer to make a 4-wire resistance measurement. The experimental cell was put in a vacuum chamber immersed in a helium bath held at 1.8–4.2 K. The heat exchange gas inside the chamber was absorbed by a charcoal cryopump to a pressure of 10^{-7} Torr. The cryopump was equipped with a heater to desorb some exchange gas when necessary to cool the sample during the experiment. Magnetic field up to 120 kOe generated by a cryomagnet was applied perpendicular to the $\langle 1\,1\,1 \rangle$ axis.

In the main part of the experiment, the temperature of the sample was measured in a quasi-adiabatic regime as a function of time and magnetic field at a sweep rate of 10 kOe/min. The corresponding temperature versus field records for different starting temperatures are shown in Fig. 1. The temperature drop during demagnetization T_i/T_f depends on the starting temperature with a maximum around $T_i \approx 10$ K where it exceeds a factor of 10. A characteristic feature for all the $T_S(H)$ curves starting below 10 K is that a significant part of cooling occurs in the field range from 120 to 60 kOe, which contrasts sharply with a continuous adiabatic cooling (T/H = constant) of an ideal paramagnet. The minimum temperature reached experimentally on demagnetization from $T_i = 2$ K at $H = 62$ kOe is $T_{min} = 0.48$ K. This cooling limit is associated with the magnetic entropy freezing at the transition into an ordered state. When the field is further decreased, a weak temperature increase is observed. Two temperature plateaus (shown by the arrows in the inset of Fig. 1) are clearly seen in this part of the curve corresponding to the phase transitions at $T_{N1} \approx 1$ K and $T_{N2} \approx 0.75$ K in coincidence with previously obtained results [4,9].

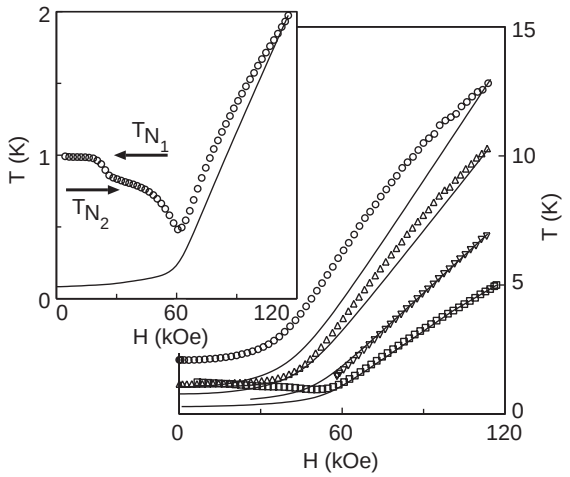

Fig. 1. Temperature variations for the adiabatic demagnetization of $Gd_2Ti_2O_7$ started at different temperatures; solid lines are obtained by MC simulations with the exchange constant $J = 0.3$ K. The inset shows separately the adiabatic curve starting at the lowest initial temperature $T_i = 2$ K.

For a quantitative description of the above experimental data we have performed a series of classical MC simulations using simplified models, which take into account only the nearest-neighbor exchange (for details see Ref. [6]). The only parameter required to compare the MC simulations to the experimental data is the exchange constant J. Its estimation from values of the saturation field or the Curie–Weiss temperature (taken from previous works [2,4,9]) gives $J = 0.3$ K. The best agreement with the experiment is achieved for the scans starting at temperatures in the intermediate range $2\,K < T_i < 10\,K$. For high-temperature curves the coincidence is worse due to a large phonon contribution to the total heat capacity of the sample. Since a nearest-neighbor Heisenberg pyrochlore antiferromagnet does not order, the MC simulations cannot describe properly

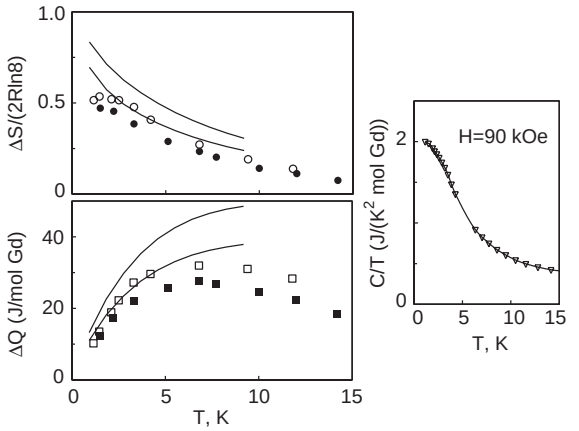

Fig. 2. The entropy change (upper left panel) and the cooling power (lower left panel) of $Gd_2Ti_2O_7$ under isothermal demagnetization from $H_i = 90\,\text{kOe}$ to $H_f = 0$ (open symbols) and from $H_i = 90\,\text{kOe}$ to $H_f = 40\,\text{kOe}$ (closed symbols); solid lines are MC calculations. Right panel: the temperature dependence of the specific heat at $H = 90\,\text{kOe}$.

the observed behavior at temperatures close to the transition point $T_{N1} = 1\,\text{K}$. The heating of the $Gd_2Ti_2O_7$ sample observed below H_{sat} at low temperatures (see the inset of Fig. 1) may be attributed to a reopening of a gap in the excitation spectrum caused by weak relativistic interactions.

Finally, we estimate the cooling power of the demagnetization process using the measured adiabatic $T_S(H)$ curves along with the specific heat data $C(T)$ obtained by quantum design PPMS calorimeter at $H = 90\,\text{kOe}$. The amount of heat absorbed by a magnetic material during isothermal demagnetization is related to the entropy change $\Delta Q = T\Delta S|_{H_i}^{H_f}$. The entropy along the adiabatic demagnetization curve $T_S(H)$ starting at (H_i,T_i) and ending at (H_f,T_f) remains constant, so one can relate the entropy variations at constant temperature and in constant field

$$\Delta S(T_f)|_{H_i}^{H_f} = \Delta S(H_i)|_{H_i}^{H_f} = \int_{T_f}^{T_i} C(T)/T\,dT \qquad (1)$$

The values of ΔS calculated from our experimental data at various temperatures using the above equation are presented in Fig. 2. Two features should be emphasized: (i) about one half of the total magnetic entropy $2R\ln 8$ remains in the system even at temperatures very close to the transition into an ordered state at $T_{N1} = 1\,\text{K}$; (ii) the largest entropy change ΔS and, consequently, a heat absorption ΔQ falls on a high field region above H_{sat}. This differs significantly from the behavior of an ideal paramagnet at low temperatures, which releases a significant part of its entropy only if demagnetized to $H_f \ll T$. The results of MC simulations shown on the same plot, reproduce the experiment with a remarkable accuracy of 10–20% even despite that the classical model cannot give correct values for the total entropy of a quantum spin system. The cooling power ΔQ has a maximum around 6 K reaching 30 J/mol Gd which is equivalent to the evaporation of approximately 1.5 mol of liquid ^{3}He at $T = 3\,\text{K}$. The garnet compound $Gd_3Ga_5O_{12}$ is also an effective refrigerant material [7]. Its behavior is qualitatively the same as that of $Gd_2Ti_2O_7$, but the enhanced cooling occurs at lower fields and temperatures due to three times smaller exchange constant $J = 0.1\,K$. We suggest that a combination of the two compounds might become the basis for a two-stage refrigerator suitable for cooling from $T \propto 10\,\text{K}$ down to 100 mK range.

In conclusion, a large magnetocaloric effect is observed in the frustrated pyrochlore antiferromagnet $Gd_2Ti_2O_7$ in agreement with recent theoretical predictions [6]. This observation points to the presence of a macroscopic number of local low-energy excitations below H_{sat}. Such modes can be directly probed in quasielastic neutron-scattering measurements analogous to the experiment on $ZnCr_2O_4$ [5]. A comparison between our experimental data and classical MC simulations shows that this numerical technique can quantitatively predict the magnetocaloric properties of real rare-earth materials with large (semiclassical) magnetic moments.

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