Frustrated Magnets as Magnetic Refrigerants

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We discuss the thermodynamics of geometrically frustrated antiferromagnets when used as refrigerants for magnetic cooling. Strong magnetic interactions, high densities of spins and yet suppressed ordering temperatures allow them to cool with demagnetization faster than conventional dilute paramagnets do. We have performed adiabatic demagnetization of a sample of gadolinium gallium garnet, $Gd_3Ga_5O_{12}$, from field $B_i = 8.0$ T to $B_f = 1.6$ T that resulted in cooling from $T_i = 1.4$ K to $T_f = 0.1$ K.

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1. Introduction

Refrigeration by means of adiabatic demagnetization of a paramagnetic salt is the oldest technique of reaching millikelvin temperatures.[1] Because of the relative technological simplicity and independence of gravity it steadily attracts attention as a rival to the dilution refrigerator.[2,3]

In the simplest idealized case, a sample containing non-interacting magnetic moments has entropy $S(B,T)$ being a function of the ratio B/T,

$$S(B,T) = f\left(\frac{B}{T}\right). \tag{1}$$

Assuming perfect thermal insulation and neglecting the entropy of phonons, etc. the temperature T is thus proportional to the magnetic field B,

$$T(B) = T_i \, \frac{B}{B_i} \, , \tag{2}$$

where T_i and B_i are the initial temperature and field. Inevitable heat leaks and extra non-magnetic contributions to the entropy cause the temperature

to change slower than proportionally to the magnetic field. The higher the density of magnetic moments n and quantum spin number J, the greater the magnetic entropy S and thus the sample can absorb more heat.

With increased density of spins, however, the strength of magnetic interactions grows. They cause magnetic ordering or formation of a spin glass at some temperature T_c, below which the technique does not work as the entropy is frozen out. Even at temperatures above T_c the cooling is less efficient because the entropy is reduced,

$$S(B,T) = f\left(\frac{[B^2 + B_{\rm int}^2]^{1/2}}{T}\right), \tag{3}$$

where the parameter $B_{\rm int}$,"internal field," is a measure of the interactions in the material.[2] Assuming no loss of entropy we again have temperature decreasing *slower than proportionally* to the decreasing magnetic field

$$T(B) = T_i\,\frac{(B^2 + B_{\rm int}^2)^{1/2}}{(B_i^2 + B_{\rm int}^2)^{1/2}}\ . \tag{4}$$

Thus, to obtain the necessary limiting temperature, one should seek a compromise between the density of spins and interactions. This is normally achieved by diluting magnetic materials with non-magnetic molecules like H_2O. To reach temperature about 100 mK, a commonly used example is ferric ammonium alum (FAA), $Fe(NH_4)(SO_4)_2 \cdot 12\ H_2O$, with $J = 5/2$, $n = 3.55 \cdot 10^{-3}$ mol cm^{-3} and $B_{\rm int} \approx 50$ mT, $T_N = 26$ mK. Because of the added H_2O, these materials are prone to dehydration at room temperature and should be kept in sealed containers.

There exists another class of spin systems, which have a potential for magnetic refrigeration. These are so-called frustrated antiferromagnets. They have a high density of spins placed on sites of special frustrated lattices. Frustration prevents magnetic ordering even at temperatures much lower than the Curie-Weiss constant and leaves a finite entropy in the disordered phase.[4] Examples of such systems include garnets ($Gd_3Ga_5O_{12}$), pyrochlores ($Gd_2Ti_2O_7$), and kagomé antiferromagnets ($SrCr_8Ga_4O_{19}$). Among them gadolinium gallium garnet (GGG) with $J = 7/2$ and $n = 1.42{\cdot}10^{-2}$ mol cm^{-3} was discussed for the purpose of magnetic refrigeration as early as the mid-seventies.[5,6] The experiments performed on single crystals at temperatures comparable to the Curie-Weiss temperature ($\Theta_{CW} = -2.3$ K) have indeed shown a very fast temperature decrease, which origin remained unclear at that time. In the present work we develop a simple theory based on the idea of frustration, which predicts a fast temperature decrease on adiabatic demagnetization for all highly frustrated magnets. We also present our results of adiabatic demagnetization on high quality polycrystalline samples of GGG to test the predictions.

2. Theoretical

Large values of spin of Gd^{3+} ions ($J = 7/2$) allow us to simplify the problem and consider the finite-field behaviour of a classical spin model. Geometrically frustrated magnets have a macroscopically degenerate ground state in zero magnetic field, because the minimum energy constraint fails to select a single classical configuration.[4] The exchange interaction constant I sets the saturation magnetic field $B_c = 6IJ$ (for garnet and kagomé antiferromagnets) or $8IJ$ (for pyrochlores). Below B_c, the external magnetic field still does not lift the degeneracy of the ground state; while above B_c the minimum energy is reached for a single configuration with parallel alignment of all spins in the direction of field.[7] Let us consider magnetic excitations at $B \geq B_c$. The spin system has two degrees of freedom per classical spin or, in total, $2n$ modes (n is the density of spins). In the saturated phase all magnetic excitations have finite energies. At $B = B_c$, when the transition takes place, some of these energies vanish. In contrast to ordinary nonfrustrated spin systems, frustrated magnets have a whole flat branch of zero-energy excitations at $B = B_c$. Their energy varies as $\varepsilon = g\mu_{\rm B}(B - B_c)$, where g and $\mu_{\rm B}$ are the g-factor and Bohr magneton, respectively. The density of such soft excitations, n_4, depends on the lattice topology and is equal to $n/5$ for the garnet lattice, $n/3$ for the kagomé lattice, and $n/2$ for the pyrochlore lattice.[7] At low temperatures and near the saturation field the most significant contribution to the thermodynamic properties is determined by such soft modes. If we denote a collective coordinate of a soft mode by y_i and of a usual harmonic mode by z_j, then the classical partition function is

$$Z = \Pi_{i,j} \int dy_i dz_j \exp\left(-\frac{g\mu_{\rm B}(B - B_c)y_i^2 + \omega_j z_j^2}{k_{\rm B}T}\right) \simeq \frac{T^n}{[g\mu_{\rm B}(B - B_c)]^{n_4/2} I^{n-n_4/2}} , \tag{5}$$

where ω_j denotes the frequency of a harmonic mode and is replaced by a constant of the order of the exchange I in the last expression. Knowing the partition function we can calculate the field dependence of the magnetic entropy,

$$S(B,T) = k_{\rm B}\left[n \ln T - \frac{n_4}{2} \ln(g\mu_{\rm B}[B - B_c])\right] . \tag{6}$$

Similar to the above analysis of the cooling rate of paramagnetic salts, we use Eq. (6) to determine temperature decrease for a frustrated magnet upon adiabatic demagnetization. It is given by

$$T(B) = T_i \left(\frac{B - B_c}{B_i - B_c}\right)^{n_4/2n} \tag{7}$$

from the initial point (B_i, T_i). The temperature decreases faster than proportionally to field, because the entropy in Eq. (6) is no longer a function of (B/T), but rather depends on the deviation from the saturation field, $(B - B_c)$. Rapid cooling is related to a simultaneous condensation of a macroscopic number of soft modes at $B = B_c$. Generally, there are different weak perturbations to the classical Heisenberg Hamiltonian, which will lift such a degeneracy on energy scales significantly lower than the exchange coupling constant. For example, these can be quantum fluctuations, next-nearest neighbour exchange, dipolar interactions, etc. Averaging over the narrow band-width of the soft modes amounts to replacing the true saturation field by some renormalized field $B_c^* < B_c$ in Eq. (7). Deviations from the above expressions should be observed at fields significantly exceeding B_c due to the neglected field-dependence of the energies of harmonic modes ω_j.

To conclude this section we note that the derived temperature reduction (7) with field is valid for all three types of frustrated magnets mentioned above. Among them, the pyrochlores, which have the largest ratio $n_4/2n$, should exhibit the fastest temperature decrease. In practice one has always to compromise by choosing the magnetic material with a suitable value of the saturation field B_c.

3. Experimental

In the rest of the paper we concentrate on our experimental results for GGG. The sample was a cylinder (diameter 5 mm, length 38 mm, mass 4.05 g) of a sintered powder GGG suspended vertically *in vacuo* on six cotton threads, each about 3 cm long. This was surrounded by a vacuum can immersed in a ^{4}He bath pumped to $T = 1.3 - 1.4$ K. A superconducting magnet around the vacuum can provided a vertical magnetic field uniform to within ± 2 % along the sample. No correction for the demagnetization factor is given here. Two thick-film commercial RuO_2 resistors (Phillips 4.7 kOhm and Neohm 1 kOhm) to act as thermometers and a thin-film strain gauge as a heater were attached to the sample with vacuum grease; ten manganin wires (diameter 70 μm, length 30 cm) provided electrical connections to the feedthrough in the vacuum can. The sample temperature is taken from the calibration of the Philips thermometer for the range 0.1 - 4.2 K after correction for the magnetic field.

In our current set-up, it was virtually impossible to pump out all exchange gas (^{4}He) after precooling to the initial temperature as low as 1.3 K. This means that the first steps of demagnetization were not performed under truly adiabatic conditions. Fortunately, after the sample reached about

0.7 K, the exchange gas quickly froze out on its surface (as monitored by a helium leak detector pumping on the vacuum can). The heat of adsorbing ^{4}He caused further increase of the sample entropy at these temperatures, but below 0.7 K the sample was already well thermally insulated.

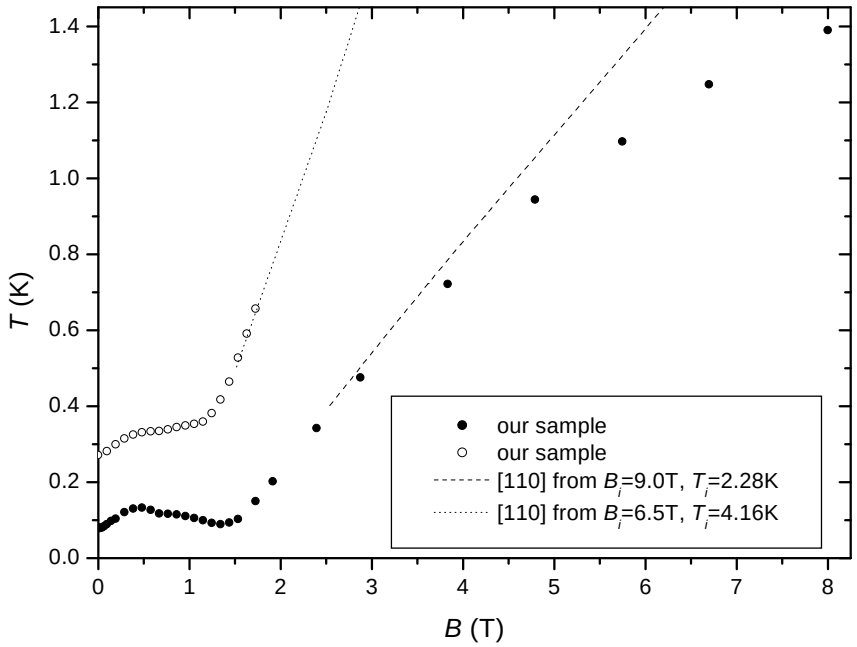

Fig. 1. Experimental temperature vs. magnetic field for two quasi-adiabatic demagnetizations of the sample of GGG (see text). Dotted and dashed lines show similar results for single crystals of GGG at higher temperatures.[5]

In Figure 1 the experimental temperatures vs. magnetic field for two runs are shown. Note that below $B_c \approx 1.6$ T and at $T < 0.4$ K GGG makes a transition into a magnetically ordered state (see [8] and references therein).

For comparison the results of adiabatic demagnetization[5] of single crystals of GGG (magnetic field along the [110] axis) available down to 0.4 K are shown in Figure 1 for two starting conditions: $B_i = 9.0$ T at $T_i = 2.28$ K and $B_i = 6.5$ T at $T_i = 4.16$ K. At temperatures below 0.7 K they are in good agreement with our results. One can conclude that, having proper thermal insulation, we could reach the same final temperature of $T_f = 100$ mK at $B_f = 1.6$ T if started from field of only $B_i \approx 6$ T at $T_i = 1.4$ K.

The experimental plots of $T(B)$ at $B > 1.5$ T qualitatively resemble the predictions of Eq. (7). The fact that they do not quite hit $T = 0$ at B_c [as would follow from Eq. (7)] is explained by deviations from ideal classical Heisenberg behaviour, with the dipolar interactions being the most prominent extra perturbation relevant for GGG. This is why the direct quantitative comparison of the experimental data with the predictions of our simplified model for $B \to B_c$ is impossible.

4. Conclusion

We have demonstrated, both theoretically and experimentally, that frustrated magnets at magnetic fields $B > B_c$ have greatly enhanced entropy which causes them to cool adiabatically with demagnetization *faster* than "conventional paramagnets."

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