Heat capacity of the frustrated magnetic pyrochlores $Gd_2Zr_2O_7$ and $Gd_2Hf_2O_7$

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Heat capacity of the frustrated magnetic pyrochlores $Gd_2Zr_2O_7$ and $Gd_2Hf_2O_7$

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Abstract

The heat capacities of $Gd_2Zr_2O_7$ and $Gd_2Hf_2O_7$ both show sharp peaks in the vicinity of 0.77 K, consistent with the existence of long range magnetic order. They are superimposed in both cases on broader maxima centered at approximately 1 K, presumably due to short range spin correlations. Both compounds exhibit antiferromagnetic interactions, with Weiss constants of approximately −7 K. Comparisons are made to earlier results for the isomorphic compounds $Gd_2Ti_2O_7$ and $Gd_2Sn_2O_7$.

1. Introduction

The insulating rare earth pyrochlores $R_2M_2O_7$ have been the object of much recent study because the magnetic rare earth ions form a cubic lattice of corner-sharing tetrahedra, an arrangement that is particularly prone to frustration. Axial moments with ferromagnetic interactions have been observed to form spin ice [1, 2], while planar and isotropic moments are frustrated when interactions are antiferromagnetic [3]. For the special case of isotropic spins with nearest-neighbor antiferromagnetic exchange, theoretical calculations have predicted no long range order as temperature approaches zero but instead a fluctuating collective paramagnetic state [4, 5].

Of the real pyrochlore materials studied to date, perhaps the closest approximations to the model isotropic antiferromagnet on a pyrochlore lattice are $Gd_2Ti_2O_7$ (GTO) and $Gd_2Sn_2O_7$ (GSO), both of which, however, order magnetically in the vicinity of 1 K, with GTO exhibiting a second ordering transition at 0.75 K [6–8]. The Curie–Weiss constant θ_W is approximately −9 K for both, resulting in a frustration parameter $|\frac{\theta_W}{T_C}| \approx 10$; the long range order has been described as resulting from a combination of further-neighbor exchange [9], dipole–dipole interaction [5], and possibly residual single-ion anisotropy in the Gd^{3+} ion [10]. In spite of these similarities, the ordered ground states of the two systems have been found to be different. GTO possesses a ground state with ordering vector $k = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ [11, 12], while GSO orders in the so-called Palmer–Chalker state with $k = (000)$ [13].

In an effort to study additional systems approximating the model Heisenberg antiferromagnet on a pyrochlore lattice, and to identify any common features, we have measured the heat capacity and susceptibility of the isostructural pyrochlores $Gd_2Zr_2O_7$ (GZO) and $Gd_2Hf_2O_7$ (GHO).

2. Experimental details

Polycrystalline samples were prepared by grinding and mixing the relevant metal oxides in stoichiometric ratio, packing the mixture into pellets, and firing for 24 h at 1650 °C, then for 72 h at 1500 °C, below the phase boundary separating the pyrochlore phase from the high temperature disordered fluorite structure [14–16]. The samples were then reground and the process repeated, followed by a final anneal for 72 h each at 1400 and 1300 °C. Powder x-ray diffraction spectra displayed the expected pyrochlore superlattice peaks, consistent with space group $Fd\bar{3}m$, and yielded lattice constants of $a = 1.0522$ nm in $Gd_2Zr_2O_7$, $a = 1.0489$ nm in $Gd_2Hf_2O_7$. Both are in reasonable agreement with previously published values [17]. Heat capacities were measured on thin samples of order 100 μg in a Quantum Design PPMS calorimeter using a ^{3}He refrigerator. Based on measurements of samples of different mass, we estimate the specific heat magnitude to be accurate to within 5%. Temperature measurements are estimated to be accurate to within 2%. Magnetic susceptibilities were measured using a MPMS squid magnetometer in a field of 500 Oe above 1.8 K.

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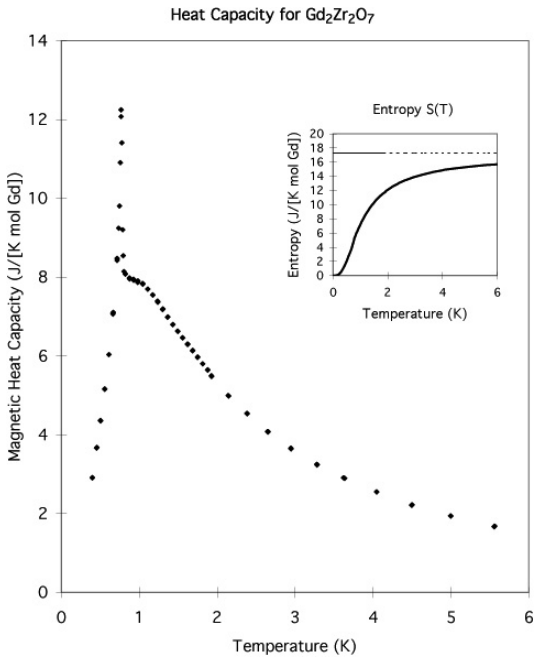

Figure 1. Magnetic specific heat of $Gd_2Zr_2O_7$ as a function of temperature below 6 K. An apparent long range order peak is visible with a maximum at 0.769 K, superimposed on a broader maximum centered at approximately 1 K, due presumably to short range correlations. The entropy $S(T)$, obtained as described in the text, is shown as an inset. The dashed line corresponds to the full spin entropy $S = R\ \ln 8$.

3. Data and analysis

The magnetic heat capacity of GZO, obtained by subtracting off the lattice T^3 contribution, is plotted in figure 1. It exhibits a broad maximum centered around approximately 1 K. Superimposed on the low temperature side of this feature is a sharp peak, consistent with a phase transition to long range magnetic order, with a maximum located at $T_c = 0.769$ K. The magnitude of the ordering peak is slightly less than the mean-field prediction of 20.4 J mol^{-1} K^{-1} for a second-order phase transition for an ion with $S = 7/2$, [18], so that, unlike GSO [8], there is little evidence of strongly first-order character in the transition. The magnetic entropy $S(T)$, shown in the inset to figure 1, was estimated by extrapolating the specific heat to $T = 0$. A linear extrapolation was used from $T = 0.4$ K down to $T = 0.27$ K, with a T^3 extrapolation below that temperature, with the requirement that the two curves match in value and slope at their common point. The entropy released up through the ordering feature is only 35% of the total magnetic entropy R ln8, shown in the inset as a dashed line, so that substantial entropy is contained in the short range correlations above T_c.

Above about 5 K, CT^2 is approximately constant at 115 J K mol^{-1}. The contribution to this from magnetic dipole–dipole interactions can be calculated [19, 20]:

$$\frac{C_{\rm dip}T^2}{R} = \frac{\left[g^2\mu_{\rm B}^2 J(J+1)\right]^2}{3k_{\rm B}^2}\sum_j \frac{1}{r_{ij}^6}, \tag{1}$$

where the lattice sum is over magnetic ions. From the lattice sum of Blote *et al* [21], we obtain $C_{\rm dip}T^2 = 11.285$ J K mol^{-1}, about 10% of the total. After subtracting off this dipolar contribution, the remaining heat capacity is due to exchange. We infer a value for the exchange constant $J_{\rm ex}$ from the isotropic mean-field result

$$\frac{C_{\rm ex}T^2}{R} = \frac{2nS^2(S+1)^2J_{\rm ex}^2}{3k_{\rm B}^2}, \tag{2}$$

yielding $J_{\rm ex}/k_{\rm B} = -0.112$ K for GZO. This can be compared with an independent determination from the paramagnetic susceptibility of GZO, shown in figure 2. The paramagnetic Weiss constant measured above 5 K is $\theta_{\rm W} = -7.7 \pm 0.5$ K. Using the isotropic mean-field result

$$\theta_{\rm W} = 2nS(S+1)J_{\rm ex}/3k_{\rm B}, \tag{3}$$

we obtain $J_{\rm ex}/k_{\rm B} = -0.122$ K, in reasonable agreement with the heat-capacity value. From the Curie constant of GZO we obtain a Gd^{3+} g factor of 1.97 ± 0.04 ($\mu_{\rm eff} = 7.83\mu_{\rm B}$), slightly

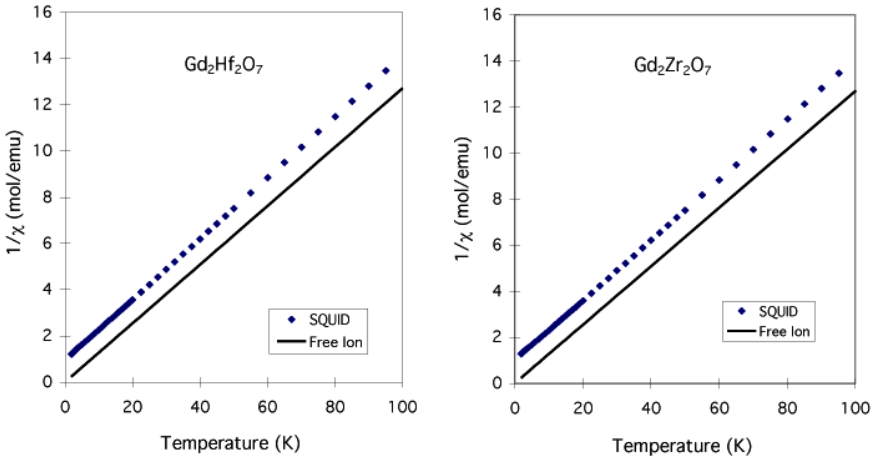

Figure 2. Inverse magnetic susceptibilities of $Gd_2Zr_2O_7$ (right) and $Gd_2Hf_2O_7$ (left) as a function of temperature. The solid lines are the free ion prediction. For GZO, the Curie–Weiss fit yields $\mu_{\rm eff} = 7.83\ \mu_{\rm B}$, and $\theta_{\rm W} = -7.7$ K. For GHO, $\mu_{\rm eff} = 7.80\ \mu_{\rm B}$, $\theta_{\rm W} = -7.3$ K.

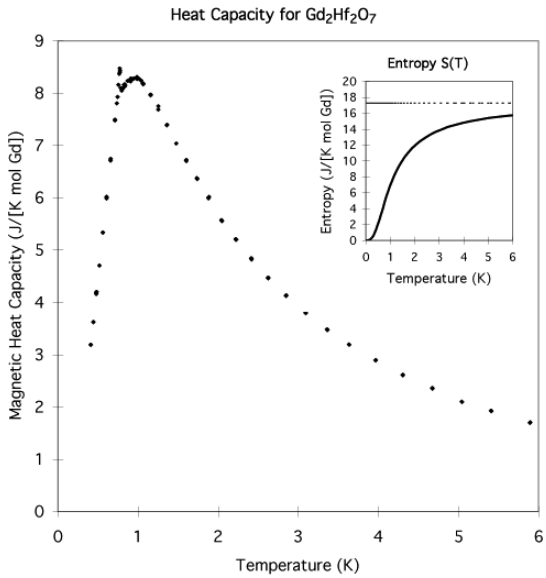

Figure 3. Magnetic specific heat of $Gd_2Hf_2O_7$ as a function of temperature below 6 K. A long range order peak, reduced in magnitude compared to GZO, is visible with a maximum at the nearly identical temperature of 0.771 K.

less than the free ion value of $g = 2.00$. In GZO and GHO, for the approximately spherical samples used, θ_W is due entirely to exchange, because the lattice is cubic and the Gd^{3+} moment is isotropic. The frustration parameter $|\frac{\theta_W}{T_C}| \approx 10$ in GZO, very similar to both GTO and GSO.

Somewhat similar comments apply to the magnetic heat capacity of GHO, which is pictured in figure 3. Here the ordering peak has a maximum at $T_c = 0.771$ K, a temperature virtually identical with GZO. The magnitude of the peak is smaller, however. This is reflected in the entropy released up to the ordering transition, which is also smaller at 32% of $R \ln 8$. The magnitude of the short range correlation anomaly around 1 K is also visibly larger in GHO than in GZO. As in GZO, there is little evidence from the heat capacity of strong first-order character in the magnetic transition. Above approximately 5 K, CT^2 is nearly constant at 125 J K mol^{-1}, yielding $J_{ex}/k_B = -0.117$ K in GHO. This agrees very well with the paramagnetic value $J_{ex}/k_B = -0.116$ K obtained from the Weiss constant $\theta_W = -7.3 \pm 0.8$ K, derived from the susceptibility of GHO shown in figure 2. The Curie constant of GHO yields a Gd^{3+} g factor of 1.966 ± 0.04, or $\mu_{eff} = 7.80\mu_B$.

GZO has been reported to exhibit disorder at elevated temperature, including superionic conductivity of the oxide ions [15], as well as appreciable cation disorder [17]. Indeed, a previous measurement of heat capacity in GZO [22] showed no long range order peak at all, only the broad short range correlation maximum. The level of disorder observed in GHO has been reported to be substantially lower than in GZO [17]. It is therefore somewhat surprising that we observe a larger long range order peak in the heat capacity of GZO, and a smaller entropy associated with short range correlations above T_c, than in GHO. It is apparent that sample preparation, particularly the extended annealing schedule, is critical to observing long range order in these rather refractory materials.

4. Discussion and conclusions

In comparing these results with the heat capacities of GTO and GSO, the ordering peaks have magnitudes much closer to that of GTO (except for the absence of a double transition) than GSO. It is possible that this is related to the reportedly higher level of structural disorder in GTO than GSO [8]. The frustration parameter $|\frac{\theta_W}{T_C}| \approx 10$ in all four materials, which is remarkable given the range in lattice constants, from 1.018 nm in GTO to 1.052 nm in GZO. The presence of persistent spin dynamics at temperatures well below T_C has been documented in GTO [23, 24] and GSO [25]. This has been related to the power-law behavior of the heat capacity below the long range order peak, which is approximately T^2 (rather than T^3, as expected for gapless spin waves) in GSO down to 0.4 K; at lower temperatures it changes to an exponential behavior indicative of a gap [8, 26]. In GZO and GHO the exponent of the power-law below T_C is roughly 1.8, which may also suggest persistent spin dynamics. The determination of the ground states of GZO and GHO, and whether they resemble those of GTO or GSO, is not provided by the heat capacity, and must await further work.

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References

[1] Ehlers G, Cornelius A L, Fennell T, Koza M, Bramwell S T and Gardner J S 2004 *J. Phys.: Condens. Matter* **16** S635
[2] Ramirez A P 1999 *Nature* **399** 333
[3] Bramwell S T and Harris M J 1998 *J. Phys.: Condens. Matter* **10** L215
[4] Villain J 1979 *Z. Phys.* B **33** 31
[5] Palmer S E and Chalker J T 2000 *Phys. Rev.* B **62** 488
[6] Raju N P, Dion M, Gingras M J P, Mason T E and Greedan J E 1999 *Phys. Rev.* B **59** 14489
[7] Ramirez A P, Shastry B S, Hayashi A, Krajewski J J, Huse D A and Cava R J 2002 *Phys. Rev. Lett.* **89** 067202
[8] Bonville P, Hodges J A, Ocio M, Sanchez J P, Vuilliet P, Sosin S and Braithwaite D 2003 *J. Phys.: Condens. Matter* **15** 7777
[9] Reimers J N, Berlinsky A J and Shi A C 1991 *Phys. Rev.* B **43** 865
[10] Glazkov V N, Smirnov A I, Sanchez J P, Forget A, Colson D and Bonville P 2006 *J. Phys.: Condens. Matter* **18** 2285
[11] Champion J D M, Wills A S, Fennell T, Bramwell S T, Gardner J S and Green M A 2001 *Phys. Rev.* B **64** 140407(R)
[12] Stewart J R, Ehlers G, Wills A S, Bramwell S T and Gardner J S 2004 *J. Phys.: Condens. Matter* **16** L321
[13] Wills A S, Zhitomirsky M E, Canals B, Sanchez J P, Bonville P, Dalmas de Reotier P and Yaouanc A 2006 *J. Phys.: Condens. Matter* **18** L37
[14] Duran P 1977 *Ceramurg. Int.* **3** 137
[15] Catchen G L and Rearick T M 1995 *Phys. Rev.* B **52** 9890
[16] Stanek C R and Grimes R W 2002 *J. Am. Ceram. Soc.* **85** 2139

[17] Shlyakhtina A V, Knotko A V, Boguslavskii M V, Stefanovich S Yu, Kolbanev I V, Larina L L and Shcherbakova L G 2007 *Solid State Ion.* **178** 59
[18] Stanley H E 1972 *Introduction to Phase Transitions and Critical Phenomena* (Oxford: Clarendon)
[19] Van Vleck J H 1937 *J. Chem. Phys.* **5** 320
[20] Daniels J M 1953 *Proc. Phys. Soc.* A **66** 673
[21] Blote H W J, Wielinga R F and Huiskamp W J 1969 *Physica* **43** 549
[22] Lutique S, Javorsky P, Konings R J M, Krupa J-C, van Genderen A C G, van Miltenberg J C and Wastin F 2004 *J. Chem. Thermodyn.* **36** 609
[23] Yaouanc A, Dalmas de Reotier P, Glazkov V, Marin C, Bonville P, Hodges J A, Gubbens P C M, Sakarya S and Baines C 2005 *Phys. Rev. Lett.* **95** 047203
[24] Dunsiger S R, Kiefl R F, Chakhalian J A, Greedan J E, MacFarlane W A, Miller R I, Morris G D, Price A N, Raju N P and Sonier J E 2006 *Phys. Rev.* B **73** 172418
[25] Bertin E, Bonville P, Bouchard J-P, Hodges J A, Sanchez J P and Vuilliet P 2002 *Eur. Phys. J.* B **27** 347
[26] Quilliam J A, Ross K A, Del Maestro A G, Gingras M J P, Corruccini L R and Kycia J B 2007 *Phys. Rev. Lett.* **99** 097201