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Single-crystal versus polycrystalline samples of magnetically frustrated $Yb_2Ti_2O_7$: Specific heat results

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Zero-field specific heat C_p measurements carried out between 0.07 and ~4 K for single crystal and powder samples of the pyrochlore $Yb_2Ti_2O_7$ display striking qualitative differences. While the powder sample has a sharp C_p anomaly at ~0.25 K, the data for the single crystals do not exhibit any sharp structure in $C_p(T)$. These results call for a cautious interpretation of microscopic results, such as those obtained by single crystal neutron scattering.

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The family of insulating rare-earth cubic (space group $Fd\bar{3}m$) compounds for which the magnetic rare-earth sublattice is composed of corner-sharing tetrahedra exhibits a rich variety of magnetic ground states.[1] This geometry is found for the pyrochlore structure. For example, when the rare-earth magnetic ions are characterized by a net ferromagnetic interaction and a very strong Ising magnetic anisotropy, the anisotropy axis being fixed along the local [111] axis at each rare-earth ion, i.e., one of the diagonal of the cubic unit cell, the spin-ice ground state is formed.[2] An analogy is drawn between the direction of the rare-earth total angular momenta, the so-called spins, in a tetrahedron and the position of hydrogen relative to oxygen in water ice. Such a system is characterized by a huge magnetic degeneracy as revealed by its large residual entropy, first explained by Pauling for water ice. Such a ground state has been found for the pyrochlores $Ho_2Ti_2O_7$,[3] $Dy_2Ti_2O_7$,[4] $Ho_2Sn_2O_7$,[5] and spinel $CdEr_2Se_4$.[6] It has been predicted that the magnetic excitations of these spin-ice systems can be described as effective magnetic monopoles,[7] which are classical rather than quantum objects. Signatures of these emergent particles have been reported.[7–12] On the other hand, when the net interaction is still ferromagnetic, but the magnetic moments are small and the crystal-electric field anisotropy is of the XY type, as for $Yb_2Ti_2O_7$, a first order transition in the spin dynamics is observed with a low-temperature ground state characterized by short-range correlations.[13,14] Other examples of magnetic ground states on a pyrochlore rare-earth sublattice have been recently discussed.[1]

More specifically for $Yb_2Ti_2O_7$, which is of interest here, a long time ago it was shown that the compound displays a sharp peak in the specific heat C_p near $T_c = 0.24$ K.[15] Using Mössbauer and positive muon spin relaxation (μSR)[16] spectroscopies, the transition was found comparable to that of a gas-liquid system, in that the fluctuation rate of the 1.15 μ_B Yb^{3+} magnetic moments drops by about four orders of magnitude at T_c.[13,17]

The original $Yb_2Ti_2O_7$ studies were performed using powder samples. Because of the exotic physical properties discovered for this compound, it is natural to extend the measurements to single crystals since large crystals of the pyrochlore titanates can be grown. One of the first steps is obviously to perform elastic neutron scattering measurements. Some of us were involved in this type of work.[18] Further investigations appeared more recently.[19–21] In zero field, rods of magnetic diffuse scattering along the [111] direction are observed. These rods are the signature of strong two-dimensional short-range correlations in a plane perpendicular to [111]. Surprisingly, the scattering features change only slightly as the sample is cooled from 0.8 down to 0.03 K, that is, when crossing T_c.[19] The two-dimensional short-range correlations above T_c seem to transform into three-dimensional short-range correlations at 0.03 K. However, under a modest 0.5 T magnetic field applied along the $[1\bar{1}0]$ direction, the short-range correlations give way to a three-dimensional long-range magnetic order.

After the publication of the first neutron results recorded with a crystal (hereafter labeled as crystal #1) and reported in Ref. 18, we carried out C_p measurements on this crystal. In Fig. 1, we plot $C_p(T)$. In sharp contrast to the powder sample, no sharp peak is observed for the crystal. Both specific heat data set were recorded in a ^{3}He-^{4}He dilution refrigerator, using a dynamic adiabatic method with a homemade calorimeter (see, e.g., Ref. 22).

In order to test the robustness of the crystal specific heat, a new crystal of $Yb_2Ti_2O_7$ was prepared in Grenoble. This crystal, labeled as #2, was grown by the traveling solvent floating zone technique (FZT) using a Crystal System Inc. optical furnace with a velocity of 8 mm per hour under air. Interestingly, our recent work on $Tb_2Ti_2O_7$ suggests a velocity of sufficiently high value to be required for producing a crystal of sufficiently good quality.[23] Indeed, for $Tb_2Ti_2O_7$ a growth velocity of 3 mm per hour yields a crystal with a C_p peak at about 0.37 K, similar to the result published by Hamaguchi *et al.* for a crystal of an unspecified growth velocity.[24] A $Tb_2Ti_2O_7$ crystal grown at high velocity does not display such a C_p peak in agreement with the other low temperature specific heat data published in the literature. As usual the physical measurements were performed on the middle part of the $Yb_2Ti_2O_7$ crystal, thus avoiding both ends which are more subject to imperfections or defects. The cell parameter was measured by x-ray diffraction using a small crushed part of the crystal, and is consistent with the powder one.

The specific heat data of the as-grown sample #2 are displayed in Fig. 1. As for the first single crystal measurement, no sharp peak is detected. As a last test of the robustness of the result, a heat treatment (HT) of crystal #2 was performed

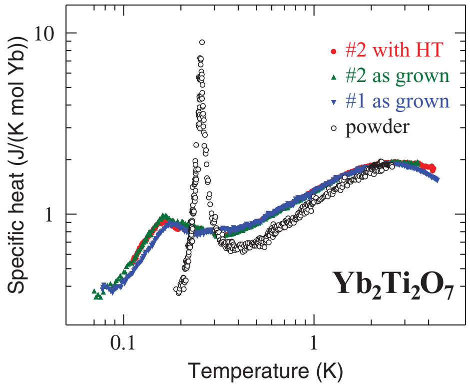

FIG. 1. (Color online) Temperature dependence of the specific heat for four samples of $Yb_2Ti_2O_7$ measured with a dilution refrigerator using a dynamic adiabatic technique. While the powder sample exhibits a sharp anomaly at about 0.25 K (Ref. 25), no such anomaly is present for the two as-grown crystals (#1 and #2), as well as heat treated crystal #2.

for 24 hours at 1100 °C under oxygen flow after which a second specific heat measurement was undertaken. This type of treatment proved to affect sizably the specific heat response of $Gd_2Ti_2O_7$.[25] As shown in Fig. 1, the three single-crystal specific heat data sets are consistent, and strictly different from the powder sample result.

Instead of the FZT adopted for the crystal growth here, one could consider the flux method which has already been used for the pyrochlore titanates.[26,27] Since the size of the crystals is then notoriously quite small, a large number of crystals would have to be produced, especially for the neutron scattering measurements. In addition, crystals grown in such a way contain a foreign element originating from the flux material.[27]

From the width of the single crystal neutron quasielastic scattering peak, a fluctuation rate for the Yb^{3+} spin of $\sim$145 GHz at 0.03 K was determined.[19] This is much higher than the rate measured by μSR with a powder sample, which is in the megahertz range.[13] As suggested by Ross *et al.*, the difference in the fluctuation rates could suggest that the spin fluctuations are characterized by two energy scales. However, the data reported in Fig. 1 question the validity of the comparison of results obtained for powders and crystals of $Yb_2Ti_2O_7$. The transition at T_c, which corresponds to a sharp change in the spin dynamics in a powder sample, simply does not seem to exist for the available crystals.

The local magnetic susceptibility was measured on a crystal of $Yb_2Ti_2O_7$.[28] These data were compared in Ref. 29 to the predictions of the anisotropic exchange interaction model of Ref. 20. Given the lack of C_p anomaly at T_c, the information inferred from the susceptibility measurement, such as the value of the spectroscopic factors, might not be relevant for comparison with results obtained on powders.[30]

As yet we do not have a definitive explanation for the origin of the differences observed in Fig. 1. As a powder sample is composed of small grains, one can imagine the oxygen atoms to easily diffuse as the sample is synthesized, and therefore these atoms would be more properly distributed in a powder sample than in a crystal. As shown in Fig. 2, a given rare-earth atom is surrounded by six oxygen ions in a buckled plane perpendicular to the local [111] direction and two oxygen ions on each side of this plane along [111]. In addition, a rare-earth ion is surrounded by a hexagon of transition metal ions. These 14 ions are expected to provide a large contribution to the crystal field at a rare-earth atom, and a slight change in their positions can influence the physical properties of the compound.

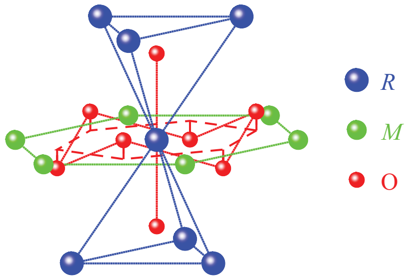

FIG. 2. (Color online) The environment of a given rare-earth atom in the pyrochlore lattice structure. We picture a rare-earth atom with the largest symbol, the oxygen atom with the smallest, and the *M* atom with an intermediate symbol size.

How can the atomic positions in a $Yb_2Ti_2O_7$ crystal be ascertained? As history shows, this is a very difficult task. The crystallographic structure of two pyrochlore compounds have attracted much interest. Let us first focus on $Tb_2Ti_2O_7$. Neutron powder-diffraction and powder x-ray-absorption fine-structure measurements indicate, within experimental error, an ideal disorder-free pyrochlore lattice.[31] In contrast, from Raman spectroscopy and terahertz time domain spectroscopy on single crystals, the presence of two nonequivalent Tb^{3+} sites in the low-temperature structure was detected.[32] High-resolution x-ray scattering measurements, also on single crystals, reveal substantial broadening and peak intensity reduction in the temperature regime 20 K to 300 mK.[33] Finally, focusing on single crystals, it has been shown that specific heat results are sample dependent.[34] The reason for the differences between different $Tb_2Ti_2O_7$ crystals is still unknown after almost ten years of intensive work.

The molybdenum pyrochlore $Y_2Mo_2O_7$ can only be prepared in a powder form. X-ray-absorption fine-structure results at the *K* edges of both Mo and Y find that the Mo-Mo pair distances are significantly disordered at approximately right angles to the Y-Mo pairs.[35] Lattice distortions have also been revealed by a nuclear magnetic resonance investigation.[36] Recently, x-ray and neutron scattering measurements indicate that the compound does not undergo any global symmetry changes. In contrast, nuclear and muon magnetic resonances studies exhibit local lattice distortions.[37] This is consistent with previous work for this compound.[35,36]

In summary, the published studies for $Tb_2Ti_2O_7$ and $Y_2Mo_2O_7$ clearly indicate that while the global cubic structure may be respected, local distortions at the ions can occur. In the case of $Yb_2Ti_2O_7$, these distortions could possibly be observed through ^{170}Yb Mössbauer, x-ray-absorption fine-structure, or ^{47}Ti nuclear quadrupole resonance studies. However, these techniques are usually applied for powder samples. No matter the origin of the specific heat differences between powder and crystal samples of $Yb_2Ti_2O_7$, it is reasonable to expect the physics of the two kinds of substances to be different. Hence, information extracted from measurements on not fully characterized single crystals[19–21,28,29] should be taken with caution.

In order to progress we propose to perform measurements on a mosaic of small crystals. Because of their restricted size, small crystals might approach the powder sample quality. Hence, the most efficient route to carry out reliable single crystal neutron investigations could be to coalign a large number of small single crystals as was done for an inelastic neutron scattering of $Tl_2Ba_2CuO_{6+\delta}$.[38] Obviously, the small crystals should first be checked by specific-heat measurements.

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