Suppression of Pauling’s Residual Entropy in Dilute Spin Ice (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$

S. Scharffe, O. Breunig, V. Cho, P. Laschitzky, M. Valldor, J. F. Welter, and T. Lorenz

$^1$II. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany
$^2$Max-Planck-Institut für Chemische Physik fester Stoffe, Noethnitzer Str. 40, 01187 Dresden, Germany

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Around 0.5 K, the entropy of the spin-ice Dy$_2$Ti$_2$O$_7$ has a plateau-like feature close to Pauling’s residual entropy derived originally for water ice, but an unambiguous quantification towards lower temperature is prevented by ultra-slow thermal equilibration. Based on specific heat data of (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$ we analyze the influence of non-magnetic dilution on the low-temperature entropy. With increasing $x$, the ultra-slow thermal equilibration rapidly vanishes, the low-temperature entropy systematically decreases and its temperature dependence strongly increases. These data suggest that a non-degenerate ground state is realized in (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$ for intermediate dilution. This contradicts the expected zero-temperature residual entropy obtained from a generalization of Pauling’s theory for dilute spin ice, but is supported by Monte Carlo simulations.

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Spin ice materials continuously attract lots of attention in current solid state physics due to their exotic ground state and anomalous excitations [1–8]. The origin of this fascinating physics arises from a geometric frustration of the magnetic interactions, which prevents long-range magnetic order down to lowest or even zero temperature. Prototype spin-ice materials are the pyrochlores with $R^3$ ions, having large magnetic moments of about 10 $\mu_B$. The magnetic ions form a network of corner-sharing tetrahedra and the crystal electric field causes a strong Ising anisotropy with local quantization axes pointing from each corner of a tetrahedron to its center. Thus, each magnetic moment is restricted to one of the $\{111\}$ directions and may point only either into or out of the tetrahedron. Antiferromagnetic exchange is so weak that the dipole-dipole interactions dominate and the energy is minimized when two spins point into and the other two point out of each tetrahedron. For a single tetrahedron, this ‘2in/2out’ ground state is 6-fold degenerate and fulfills Pauling’s ice rule describing the hydrogen distribution in water ice with the residual entropy $S_P = (N_A k_B/2) \ln(3/2)$ [9, 10]. Excitations are created by single spin flips resulting in pairs of tetrahedra with ‘3in/1out’ and ‘1in/3out’ configurations. As a consequence of the ground-state degeneracy, each pair fractionalizes into two individual excitations that can be described as magnetic (anti-)monopoles propagating independently through the lattice [3, 4, 11, 12]. The dynamics of these anomalous monopole excitations is subject of intense research [5, 13–16].

Experimental evidence for the presence of Pauling’s residual entropy in spin-ice systems stems from specific heat measurements [17–20] reporting a practically temperature-independent low-temperature entropy $S_{\infty}(T < 0.4 K) \approx S_P$. More recently, however, extremely slow relaxation phenomena were observed for Dy$_2$Ti$_2$O$_7$ in low-temperature measurements of, e.g., the magnetization [21, 22], ac susceptibility [23], thermal transport [24, 25] or the specific heat [24, 26, 27]. Typically, these phenomena set in below $\approx 0.6$ K and signal strongly increasing timescales for the internal thermal equilibration of Dy$_2$Ti$_2$O$_7$. Therefore, the specific-heat values obtained by standard relaxation-time techniques are too low and $S_{\infty}(T < 0.5 K) < S_P$ was reported for for thermally equilibrated Dy$_2$Ti$_2$O$_7$ [27]. The origin of this discrepancy remains to be clarified. Another open issue is the influence of non-magnetic dilution on the spin-ice ground state [28]. By generalizing Pauling’s approximation, a non-monotonic dependence $S_P(x)$ as a function of the dilution content $x$ was predicted and seemed roughly to be confirmed experimentally in $(R_{1-x}Y_x)_2Ti_2O_7$ for $R = Dy$ and Ho [22]. Very recent Monte Carlo (MC) simulations of dilute spin ice also find a non-monotonic $x$ dependence of the low-temperature entropy, but also reveal that for $x > 0.2$ the numerically obtained entropy $S_{MC}(x, T < 0.7 K)$ falls below the expected $S_P(x)$ and decreases further towards lower temperature [30]. A quantitative comparison to experimental data $S_{\infty}(x, T)$ was not done in Ref. [30] due to the experimental difficulties, which partly arise from the slow thermal equilibration but also from the uncertainty in estimating the phononic specific heat to high-enough temperature.

In this report, we present a detailed specific-heat study of the dilution series (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$ with $x = 0–1$. We find that the slow thermal equilibration is rapidly suppressed with increasing dilution and vanishes for $x \geq 0.2$. For all $x$, the experimentally derived $S_{\infty}(x, T < 0.5 K)$ is smaller than $S_P(x)$ and the deviation increases with $x$. The lowest-temperature ($T = 0.4$ K) Monte Carlo results also overestimate the magnetic entropy of (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$, but well match the experimental data at $T = 0.7$ K. With increasing dilution, our data clearly show a systematic increase of the temperature dependence of the low-temperature entropy such that a zero-temperature extrapolation suggests a complete suppression of the residual entropy or, in other words, a non-
The present study has been performed on oriented (DY1-xYx)2Ti2O7 samples of approx. 20 mg, which were cut from large single crystals grown by the floating-zone method in a mirror furnace. The Dy:Y ratio was checked by energy dispersive x-ray diffraction (EDX) and by analyzing the relative decrease of the low-temperature saturation magnetization. The results of both methods agree within a few percent to the nominal concentration x.

The specific heat was measured with a home-built calorimeter in the temperature range from about 0.3 to 30 K in magnetic fields of 0, 0.5, and 1 T applied along the [100] direction. In general, the standard relaxation-time method was used, but this method fails if the internal thermal equilibration becomes too slow as is the case in the low-temperature range (T < 0.6 K) of pure and weakly dilute (see below) spin ice. There, we used a constant heat-flow method analyzing the heating curve over a longer timescale [24], which is equivalent to the method of Ref. [27] where the specific heat is derived from the temperature-relaxation curve.

Fig. 1 compares typical heating curves of the normalized temperature difference 1 - ∆T(t)/∆T max where ∆T = T - T0 and T0 is the base temperature. At T0 ≃ 0.8 K, the heating curves over the entire dilution range in (DY1-xYx)2Ti2O7 are straight lines in a semi-logarithmic representation. This is expected if the internal thermal equilibration, where internal means inside the sample as well as between the sample and the platform, is much faster than the thermal relaxation to the external heat bath. The heat capacity is obtained via C = τK from the fitted relaxation time τ and from the thermal conductance K = P/ΔT max between the sample platform and the thermal bath with P denoting the heating power. For lower base temperatures T0 ≃ 0.5 K and 0.36 K, however, the relaxation curves of pure DY2Ti2O7 become non-exponential as a consequence of the slow internal thermal equilibration. In these cases, the heat capacity is obtained from the difference Q(t) = Pt - ∫ KT(t) dt between the total dissipated heat and the heat flown from the platform to the bath via C = Q(t)/ΔT(t), which approaches a constant in the long-time limit. In order to ensure measurable variations in ΔT(t) over long times, the thermal coupling K has to be weak enough. The setup used here allows for measurements of up to ≃ 1000 s, but, according to Ref. [27], the timescales to reach thermal equilibration in DY2Ti2O7 drastically increase to several 10^4 s below ≃ 0.4 K. Thus, our lowest-temperature data significantly deviate from those of Ref. [27] but both data sets match above 0.4 K and are much larger than those obtained by the standard relaxation technique. Finally, all data sets merge above ≃ 0.6 K. Concerning the dilute (DY1-xYx)2Ti2O7 crystals, the low-temperature heating curves for x = 0.05 and 0.1 also become non-exponential, but this effect is much less pronounced than in the pure DY2Ti2O7, and for x ≥ 0.2 the heating curves remain exponential down to the lowest temperature. Thus, our data clearly show that the extremely slow thermal equilibration in the pure spin ice DY2Ti2O7 is drastically suppressed by comparatively weak dilution with non-magnetic Y.

The specific heat c of (DY1-xYx)2Ti2O7 measured in zero magnetic field is displayed in Fig. 2(a). Above ≃ 1 K, c(T) continuously decreases with increasing dilution x. Because the specific heat is dominated by its magnetic contribution c mag below ≃ 10 K, the corresponding decrease essentially reflects the decreasing amount of magnetic Dy ions with increasing x. Above 10 K, the phononic contribution c ph starts to dominate and the systematic decrease with increasing x can be traced back to the fact that Y is much lighter than Dy. The molar mass per formula unit (fu) of (DY1-xYx)2Ti2O7 decreases from 533 to 386 g/molfu between x = 0 and 1, respectively. Thus, for larger x the eigenfrequencies of the acoustic phonon branches are enhanced and the low-temperature increase of c ph sets in at higher temperature. In order to estimate c ph of the Dy-containing crystals, the temperature axis of the measured c(T) of the non-magnetic Y2Ti2O7 was rescaled in such a way that it matches the specific heat of (DY1-xYx)2Ti2O7 in the temperature range around 25 K, i.e. via c ph(x,T) = (x/2) c ph(1,T = 25 K) with x-dependent scaling factors ranging from r x = 0.8 to 0.95 for 0 ≤ x ≤ 0.75, respectively. As an example, the resulting c ph of the pure DY2Ti2O7 is shown as a dashed line in Fig. 2(a) and the magnetic contributions derived via c ph mag(T) = c ph(T) - c ph(0,T) are displayed for all x ≤ 0.75 in Fig. 2(b). Here, the data are normalized to

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the amount of the magnetic Dy ions and are displayed as $c_{\text{mag}}/T$ versus $T$. In this representation, the data for all $x$ almost coincide above 2 K whereas below $\approx 0.7$ K we observe a drastic increase of $c_{\text{mag}}/T$ with increasing $x$. The latter observation means that the temperature dependence of the entropy $\partial S/\partial T = c_{\text{mag}}/T$ strongly increases with $x$ for $T < 0.7$ K. Note that this conclusion is independent from the uncertainty in estimating the phononic background because any realistic $c_{\text{ph}}$ is negligibly small compared to $c_{\text{mag}}$ in the entire temperature range of Fig. 2(b). Moreover, it is also essentially independent from the slow thermal equilibration effects, which are only present in the weakly dilute samples at very low temperatures. As can be seen in Fig. 2(b), the $c_{\text{mag}}/T$ data of thermally equilibrated Dy$_2$Ti$_2$O$_7$ show a low-temperature increase, but still remain below the corresponding data for $x \geq 0.2$.

The magnetic entropy $S(T)$ is obtained by temperature integration of $c_{\text{mag}}/T$ and requires an estimate of $c_{\text{ph}}$. Often $c_{\text{ph}}$ is estimated by a Debye model or a simple power-law, e.g. $\beta T^3 + \beta' T^5$, which match the measured total $c(T)$ around 15 K [17, 18, 29, 30]. However, the corresponding $c_{\text{mag}}$ bears several uncertainties concerning the higher temperature range, as discussed in Ref. [30]. In consequence, the obtained entropy changes for finite magnetic fields do not reach the full entropy $S_\infty = N_A k_B \ln(2)$ of a two-level system at $T = 25$ K. The red dashed lines mark the residual entropy $S_T(x)$ expected for $B = 0$ from a generalized Pauling approximation [24].

FIG. 2. (Color online) (a) Specific heat $c(T)$ per formula unit (fu) (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$ for selected $x$ with an expanded view of the low-temperature range for all $x$ in the inset. The phononic contributions $c_{\text{ph}}^p(T)$ were estimated by the specific heat of non-magnetic Y$_2$Ti$_2$O$_7$ after rescaling the temperature axis such that the data sets match around $T \approx 25$ K, as is shown for $x = 0$ by the dashed line. In (b), the resulting magnetic contribution $c_{\text{mag}}^p(T) = c(T) - c_{\text{ph}}^p(T)$ normalized by the Dy content is displayed in the representation $c_{\text{mag}}^p/T$ versus $T$ for $T \leq 2.5$ K. For Dy$_2$Ti$_2$O$_7$, $c_{\text{mag}}^p/T$ obtained either by a standard relaxation measurement (+, 24) or after extremely long-time equilibration (▲, 27) are included.

FIG. 3. (Color online) Entropy $S_\infty(T)$ of (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$ obtained by integration of $c_{\text{mag}}/T$ measured in $B = 0$, 0.5, and 1 T ||[100]. All curves are shifted to match the full entropy $S_\infty = N_A k_B \ln(2)$ of a two-level system at $T = 25$ K. The red dashed lines mark the residual entropy $S_T(x)$ expected for $B = 0$ from a generalized Pauling approximation [24].
that around 25 K the full entropy expected from a generalized Pauling approximation, and the zero-temperature residual entropy $S_T(x)$ (dashed line) expected from a generalized Pauling approximation [30].

Now we come to the main point of this study, namely the question, whether there is experimental evidence for a degenerate zero-field ground state in the dilute spin ice (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$ or, in other words, is it justified to extrapolate the derived low-temperature entropy to a finite zero-temperature residual entropy. Because of the problematic slow thermal equilibration, we restrict the following discussion to $T \geq 0.4$ K for the weakly diluted samples with $x \leq 0.1$. As is shown in the inset of Fig. 3 (a), the low-temperature entropy of pure Dy$_2$Ti$_2$O$_7$ is close to the expected $S_T$ and has a weak, but finite temperature dependence. One may interpret this approximate plateau-like feature of the entropy as one justification for the description of Dy$_2$Ti$_2$O$_7$ in terms of a spin ice down to these temperatures. It remains, however, an open issue, whether or not the remaining entropy would finally vanish towards lower temperature in a fully thermally equilibrated Dy$_2$Ti$_2$O$_7$. With increasing dilution level $x$, the experimental entropy at lowest temperatures clearly falls below $S_T(x)$ and its temperature dependence systematically increases. Nevertheless, at least for $x \leq 0.1$ a linear extrapolation $S_{ex}(x, T \to 0)$ would still yield a finite zero-temperature residual entropy, what may be interpreted as some reminiscence of spin-ice behavior. Towards larger $x$, however, the deviation between $S_T(x)$ and the experimental $S_{ex}(x, T)$ as well as the slope $\partial S_{ex}/\partial T = c_{mag}/T$ become so large that an interpretation in terms of a finite residual entropy is no longer justified. This conclusion is in strong contrast to the early interpretation of Ref. 29. At this point, we want to emphasize that $c_{mag}/T$ of Refs. 29 and 30 show a comparable low-temperature increase as our data for $x \geq 0.2$ and the strong slope of the low-temperature entropy already rules out an interpretation in terms of a finite residual entropy.

Recently, a comparison between the generalized Pauling residual entropy $S_T(x)$ and the low-temperature entropy $S_{MC}(x, T)$ from Monte Carlo simulations was reported [30]. In Fig. 4 we include the experimental low-temperature entropy $S_{ex}(x, T)$ of (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$ to the corresponding comparison of Ref. 30. As already discussed, this comparison yields that for $x \geq 0.2$ the lowest-temperature values of both, $S_{MC}(x, T)$ and $S_{ex}(x, T)$ significantly fall below $S_T(x)$, although the latter is a zero-temperature result. Moreover, we find a good quantitative agreement between the Monte Carlo and the experimental results at $T = 0.7$ K, where $S_{ex}(x, T)$ is nicely reproduced by $S_{MC}(x, T)$ in the entire dilution range $0 \leq x \leq 0.75$ of our crystals. In contrast, the lowest-temperature Monte Carlo data $S_{MC}(x, T = 0.4$ K) overestimate the experimental results and essentially reproduce the experimental $S_{ex}(x, T = 0.5$ K). Thus, an extension of the Monte Carlo simulations down to lower temperatures would be of interest. Concerning the theoretically obtained non-monotonic $x$ dependence, a shallow maximum of the entropy around $x \approx 0.2$ is also present in $S_{ex}(x, T)$ down to $T \geq 0.4$ K, while below that temperature the slow thermal equilibration for $x \leq 0.1$ prevents a definite conclusion. From $x = 0.5$ to 0.75, the entropy increases again and we think that this reflects the fact that with increasing $x$ the average dipole-dipole interaction decreases. Thus, the temperature-dependent drop of the entropy continuously shifts towards lower temperature and, as a consequence, the entropy at constant temperature continuously increases with $x$.

In conclusion, we find that the ultra-slow thermal equilibration in pure spin ice Dy$_2$Ti$_2$O$_7$ is rapidly suppressed upon dilution with non-magnetic Y and vanishes completely for $x \geq 0.2$ down to 0.3 K. In general, the low-temperature entropy of (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$, considerably decreases with increasing $x$, whereas its temperature-dependence drastically increases. Thus, there is no experimental evidence for a finite zero-temperature entropy in (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$ above $x \approx 0.2$, in clear contrast to the finite residual entropy $S_T(x)$ expected from a generalized Pauling approximation [29]. A similar discrepancy is also present between $S_T(x)$ and the low-temperature
entropy obtained by Monte Carlo simulations \cite{30}, which, at least partially, reproduce our experimental data. Our data suggest a rapid crossover from spin-ice physics in Dy$_2$Ti$_2$O$_7$ towards weakly interacting single-ion physics in (Dy$_{1-x}$Y$_x$)$_2$Ti$_2$O$_7$ at intermediate dilution.

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\[\text{E-mail: tl@ph2.uni-koeln.de}\]

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