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Suppression of Pauling's residual entropy in the dilute spin ice $(Dy_{1-x}Y_x)_2Ti_2O_7$

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Around 0.5 K, the entropy of the spin ice $Dy_2Ti_2O_7$ has a plateaulike feature close to Pauling's residual entropy derived originally for water ice, but an unambiguous quantification towards lower temperature is prevented by ultraslow thermal equilibration. Based on the specific-heat data of $(Dy_{1-x}Y_x)_2Ti_2O_7$ we analyze the influence of nonmagnetic dilution on the low-temperature entropy. With increasing x, the ultraslow thermal equilibration rapidly vanishes, the low-temperature entropy systematically decreases, and its temperature dependence strongly increases. These data suggest that a nondegenerate ground state is realized in $(Dy_{1-x}Y_x)_2Ti_2O_7$ 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 attract lots of attention due to their exotic ground state and anomalous excitations [1–8], which arise from a geometric frustration of the magnetic interactions that prevents long-range magnetic order. Prototype spin-ice materials are the pyrochlores $R_2Ti_2O_7$ with Dy or Ho as R^{3+} ions, which form a network of corner-sharing tetrahedra. 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. The energy of antiferromagnetic exchange and dipole-dipole interactions is minimized when two spins point into and the other two point out of each tetrahedron. This "2-in/2-out" ground state is sixfold degenerate and fulfills Pauling's ice rule describing the hydrogen displacement 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 "3-in/1-out" and "1-in/3-out" 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 monopole excitations is the subject of intense research [5,13–16].

Experimental evidence for Pauling's residual entropy in spin-ice systems stems from specific-heat measurements [17–20] reporting a practically temperature-independent entropy $S_{ex}(T \approx 0.4\ \mathrm{K}) \simeq S_P$. More recently, however, extremely slow relaxation phenomena were observed for $Dy_2Ti_2O_7$ 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 ≈ 0.6 K and signal strongly increasing time scales for the internal thermal equilibration. Therefore, the specific-heat values obtained by standard relaxation-time techniques are too low and $S_{ex}(T < 0.5\ \mathrm{K}) < S_P$ was reported for thermally equilibrated $Dy_2Ti_2O_7$ [27]. The origin of this discrepancy remains to be clarified. Another open issue is the influence of nonmagnetic dilution on the spin-ice ground state [28]. By generalizing Pauling's approximation, a nonmonotonic dependence $S_P(x)$ as a function of the dilution content x was predicted [29]. This was essentially confirmed by recent Monte Carlo (MC) simulations, but for $x > 0.2$ the numerically obtained entropy $S_{MC}(x,T < 0.7\ \mathrm{K})$ falls below the expected $S_P(x)$ [30]. A quantitative comparison of $S_{MC}(x,T)$ to experimental data $S_{ex}(x,T)$ 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.

In this Rapid Communication, we present a detailed specific-heat study of the dilution series $(Dy_{1-x}Y_x)_2Ti_2O_7$. We find that the slow thermal equilibration is rapidly suppressed with increasing dilution and vanishes for $x \geqslant 0.2$. For all x, the experimentally derived $S_{ex}(x,T < 0.5\ \mathrm{K})$ is smaller than $S_P(x)$ and the deviation increases with x. The lowest-temperature ($T = 0.4$ K) MC results also overestimate the magnetic entropy of $(Dy_{1-x}Y_x)_2Ti_2O_7$, but well match the experimental data at $T = 0.7$ K. With increasing dilution, our data reveal 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 nondegenerate ground state for $x > 0.2$.

Oriented $(Dy_{1-x}Y_x)_2Ti_2O_7$ samples of ≈ 20 mg were cut from large mirror-furnace grown single crystals. The Dy:Y ratio was checked by energy dispersive x-ray diffraction and from the relative decrease of the 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 from about 0.3 to 30 K in magnetic fields of 0, 0.5, and 1 T applied along [100]. 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 time scale [24], which is equivalent to the method of Refs. [27,31] where the specific heat is derived from the temperature-relaxation curve.

Figure 1 compares typical heating curves of the normalized temperature difference $1 - \Delta T(t)/\Delta T_{max}$, where

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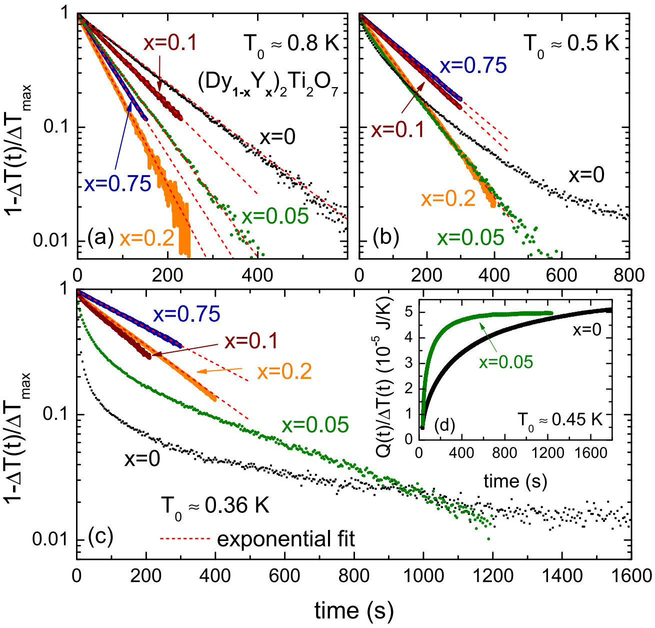

FIG. 1. (Color online) Heating curves $1-\Delta T(t)/\Delta T_{\max}$ of $(\mathrm{Dy}_{1-x}\mathrm{Y}_x)_2\mathrm{Ti}_2\mathrm{O}_7$ with $x = 0$–0.75. Here, $\Delta T(t) = T(t) - T_0$ is measured relative to the base temperature T_0 and $\Delta T_{\max}$ is its limiting value. The dashed red lines are fits to those data showing an exponential decay with a single relaxation time. (d) The heat $Q(t)$ stored in the sample divided by $\Delta T(t)$ approaches the total heat capacity C in the long-time limit.

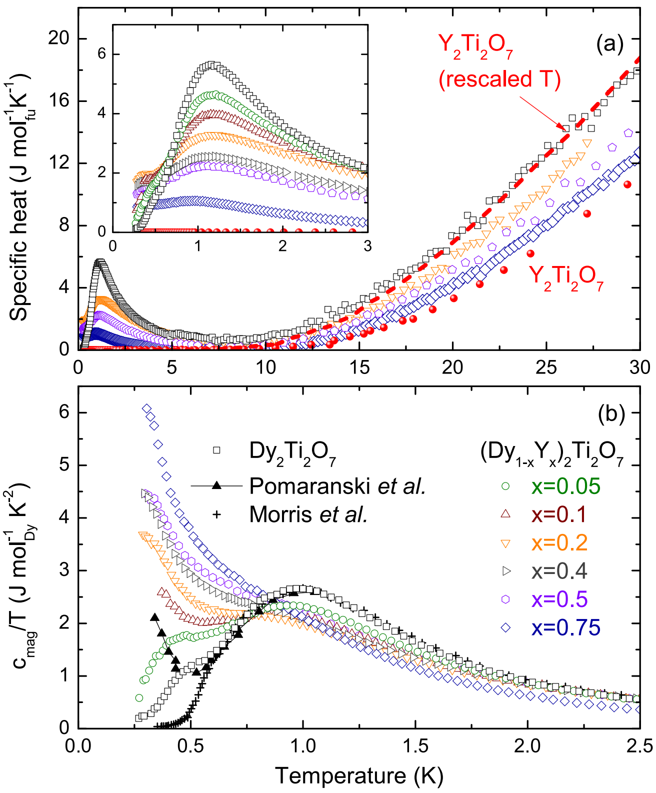

FIG. 2. (Color online) (a) Specific heat $c(T)$ per formula unit (f.u.) $(\mathrm{Dy}_{1-x}\mathrm{Y}_x)_2\mathrm{Ti}_2\mathrm{O}_7$ for selected x with an expanded view of the low-temperature range for all x in the inset. The phononic contributions $c_{\mathrm{ph}}(x,T)$ were estimated by the specific heat of nonmagnetic $\mathrm{Y}_2\mathrm{Ti}_2\mathrm{O}_7$ after rescaling the temperature axis such that the data sets match around $T \simeq 25$ K, as is shown for $x = 0$ by the dashed line. In (b), the resulting magnetic contribution $c_{\mathrm{mag}}(x,T) = c(x,T) - c_{\mathrm{ph}}(x,T)$ normalized by the Dy content is displayed in the representation c_{mag}/T vs T for $T \leqslant 2.5$ K. For $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$, c_{mag}/T obtained either by a standard relaxation measurement (+ [20]) or after extremely long-time equilibration (▲ [27]) are included.

$\Delta T = T - T_0$ and T_0 is the base temperature. At $T_0 \simeq 0.8$ K, the heating curves over the entire dilution range in $(\mathrm{Dy}_{1-x}\mathrm{Y}_x)_2\mathrm{Ti}_2\mathrm{O}_7$ are straight lines in a semilogarithmic 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 $C = \tau K$ from the relaxation time τ and the thermal conductance $K = P/\Delta T_{\max}$ between the sample platform and the thermal bath with the heating power P. For $T_0 \simeq 0.5$ and 0.36 K, however, the relaxation curves of pure $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$ become nonexponential due to slow internal thermal equilibration. In these cases, the heat capacity is obtained from the difference $Q(t) = Pt - \int K\Delta T(t)dt$ between the total dissipated heat and the heat flown from the platform to the bath via $C = Q(t)/\Delta T(t)$, which approaches a constant in the long-time limit [see Fig. 1(d)]. A weak thermal coupling K is necessary to ensure measurable variations of $\Delta T(t)$ over long-enough times, which restricts the measurements to ≈ 1000 s in the actual setup. As shown previously [24], our specific-heat data agree well with those of Ref. [26], but both data sets are significantly larger than those obtained by the standard relaxation technique [20] on $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$ for $T < 0.6$ K. Our technique and that of Ref. [26] have in common that the heat pulses are analyzed over comparable time scales of up to ≈ 1000 s. However, according to Ref. [27], the time to reach internal thermal equilibration in $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$ drastically increases to several 10^4 s below ≈ 0.4 K. Such ultraslow equilibration effects cannot be captured in a setup, whose temperature relaxes significantly faster towards that of the external heat bath. Consequently, our lowest-temperature data (as well as those of Ref. [26]) significantly deviate from the recently published specific heat of $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$ that was thermally equilibrated for much longer times [27]. As shown in Fig. 2, our data match those of Ref. [27] at ≈ 0.4 K, but exceed the data obtained by the standard relaxation technique up to ≈ 0.6 K, above which all data sets finally merge [32].

Concerning dilute $(\mathrm{Dy}_{1-x}\mathrm{Y}_x)_2\mathrm{Ti}_2\mathrm{O}_7$, the low-temperature heating curves for $x = 0.05$ and 0.1 also become nonexponential, but this effect is much less pronounced than in pure $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$, and for $x \geqslant 0.2$ the heating curves remain exponential down to the lowest temperature (see Fig. 1). Thus, our data show that the ultraslow thermal equilibration in $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$ is drastically suppressed by weak nonmagnetic dilution. This could result from a suppressed slowing down of the spin-ice dynamics due to an enhanced monopole density in weakly dilute spin ice, because the monopole creation is facilitated close to partially occupied tetrahedra [28].

The specific heat of $(\mathrm{Dy}_{1-x}\mathrm{Y}_x)_2\mathrm{Ti}_2\mathrm{O}_7$ measured in zero magnetic field is displayed in Fig. 2(a). Above ≈ 1 K,

$c(x,T)$ continuously decreases with increasing dilution x. Below ≈ 10 K, this decrease essentially reflects the decreasing amount of magnetic Dy ions, because the magnetic contribution c_{mag} dominates here. 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 (f.u.) of $(\mathrm{Dy}_{1-x}\mathrm{Y}_x)_2\mathrm{Ti}_2\mathrm{O}_7$ decreases from 533 to 386 g/mol$_{\mathrm{f.u.}}$ 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 a higher temperature. In order to estimate c_{ph} of the Dy-containing crystals, the temperature axis of the measured $c(T)$ of the nonmagnetic $\mathrm{Y}_2\mathrm{Ti}_2\mathrm{O}_7$ was rescaled such that it matches the specific heat of $(\mathrm{Dy}_{1-x}\mathrm{Y}_x)_2\mathrm{Ti}_2\mathrm{O}_7$ around 25 K, i.e., $c(x = 1, r_x T) = c(x < 1, T \simeq 25\ \mathrm{K})$ with scaling factors ranging from $r_x = 0.8$ to 0.95 for $0 \leqslant x \leqslant 0.75$, respectively. As an example, the resulting c_{ph} of pure $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$ is shown as a dashed line in Fig. 2(a) and the magnetic contributions derived via $c_{\mathrm{mag}}(x,T) = c(x,T) - c(x = 1, r_x T)$ are displayed for all $x \leqslant 0.75$ in Fig. 2(b). Here, the data are normalized to the amount of the magnetic Dy ions and are displayed as c_{mag}/T vs T. In this representation, the data for all x almost coincide above 2 K whereas a systematic low-temperature increase of c_{mag}/T evolves with increasing x. The latter observation means that the low-temperature dependence of the entropy $\partial S/\partial T = c_{\mathrm{mag}}/T$ strongly increases with x. Note that this conclusion is independent from the uncertainty in estimating the phononic background because any realistic c_{ph} is negligibly small compared to c_{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_{mag}/T data of thermally equilibrated $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$ [27] show a low-temperature increase, but still remain below the corresponding data for $x \geqslant 0.1$.

The magnetic entropy $S(T)$ is obtained by temperature integration of c_{mag}/T and requires an estimate of c_{ph}. Often c_{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_{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 $S_\infty = N_{\mathrm{A}} k_{\mathrm{B}} \ln(2) \simeq 5.76$ J/mol K, even though the fields are large enough to fully lift the ground-state degeneracy [17,18,29]. This can be avoided when c_{ph} is estimated by the measured c of a suitable nonmagnetic reference material [19]. Here, we use the temperature-rescaled c_{ph} of the nonmagnetic $\mathrm{Y}_2\mathrm{Ti}_2\mathrm{O}_7$ and check the reliability of our procedure by measuring the specific heat of all $(\mathrm{Dy}_{1-x}\mathrm{Y}_x)_2\mathrm{Ti}_2\mathrm{O}_7$ samples in $B = 0.5$ and 1 T applied along the [100] direction. For this direction, field strengths between 0.5 and 1 T are, on the one hand, sufficient to reach a fully saturated magnetization at $T \simeq 0.5$ K. On the other hand, such fields are still low enough to reach the full entropy S_∞ of a two-level system around 25 K, where the thermal population of higher-lying crystal field levels is still negligible [33,34]. Figure 3 summarizes the magnetic entropy of the series $(\mathrm{Dy}_{1-x}\mathrm{Y}_x)_2\mathrm{Ti}_2\mathrm{O}_7$. In all cases, the integration constants were adjusted by $S(25\ \mathrm{K}) = S_\infty$ and for each composition a magnetic-field independent c_{ph} was used. For all x, the low-temperature extrapolations $S(T \to 0, B \geqslant 0.5\ \mathrm{T}) \to 0$ and thus clearly confirm the expected vanishing residual entropy in finite fields.

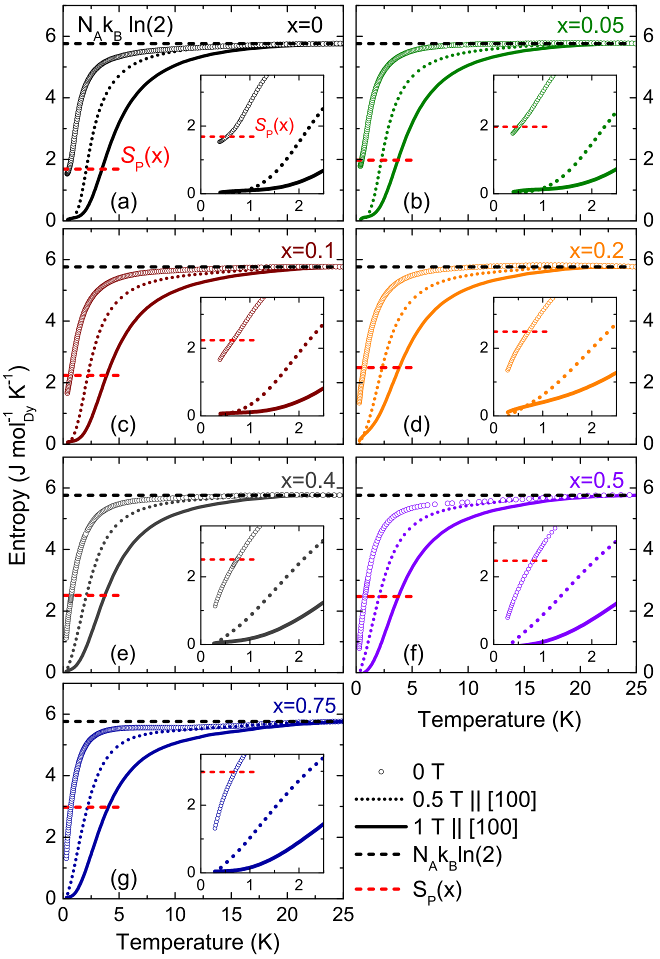

FIG. 3. (Color online) Entropy $S_{\mathrm{ex}}(T)$ of $(\mathrm{Dy}_{1-x}\mathrm{Y}_x)_2\mathrm{Ti}_2\mathrm{O}_7$ obtained by integration of c_{mag}/T measured in $B = 0$, 0.5, and 1 T $\parallel$[100]. All curves are shifted to match the full entropy $S_\infty = N_{\mathrm{A}} k_{\mathrm{B}} \ln(2)$ of a two-level system at $T = 25$ K. The red dashed lines mark the residual entropy $S_{\mathrm{P}}(x)$ expected for $B = 0$ from a generalized Pauling approximation [29].

Now we come to the question of whether there is experimental evidence for a degenerate zero-field ground state in the dilute spin ice $(\mathrm{Dy}_{1-x}\mathrm{Y}_x)_2\mathrm{Ti}_2\mathrm{O}_7$. Because of the ultraslow thermal equilibration, we restrict this discussion to $T \geqslant 0.4$ K for the weakly dilute samples with $x \leqslant 0.1$. As is shown in the inset of Fig. 3(a), the low-temperature entropy of pure $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$ is close to the expected S_{P} and has a weak, but finite, temperature dependence. This approximate plateaulike feature of the entropy is one justification for the description of $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$ in terms of a classical spin ice down to these temperatures. The finite slope, which, according to Ref. [27], further increases below 0.4 K, however, indicates that some kind of ordered ground state ultimately evolves in $\mathrm{Dy}_2\mathrm{Ti}_2\mathrm{O}_7$. One may expect this to occur due to quantum effects, additional weaker interactions, and/or magnetoelastic coupling, but the real ground states of this and other (quantum) spin-ice candidates are in most cases not known (see, e.g., Refs. [35–37]). Recently, various ordered ground states for $Dy_2Ti_2O_7$ have been suggested which can arise depending on the strength of quantum tunneling [38]. Moreover, weak nonmagnetic dilution may induce transitions to a so-called topological spin glass [28], with a gradual suppression of the residual entropy setting in at $T_c(x)$ [39].

Concerning the entropy of the dilute $(Dy_{1-x}Y_x)_2Ti_2O_7$, the plateaulike feature around 0.5 K rapidly vanishes and the temperature dependence of $S_{\mathrm{ex}}(x,T)$ strongly increases with x. Nevertheless, for $x \leqslant 0.1$, a linear extrapolation $S_{\mathrm{ex}}(x,T \to 0)$ would still yield a finite zero-temperature residual entropy, what may be interpreted as reminiscent of spin-ice behavior in this intermediate temperature range. Towards larger x, however, the slope $\partial S_{\mathrm{ex}}/\partial T = c_{\mathrm{mag}}/T$ becomes so large that an interpretation in terms of a finite residual entropy is no longer justified. For comparison with theoretical predictions, the generalized Pauling residual entropy $S_{\mathrm{P}}(x)$ from the early work of Ke *et al.* [29] is shown by the dashed lines in Fig. 3. Although $S_{\mathrm{P}}(x)$ is a zero-temperature result it is significantly larger than the experimental $S_{\mathrm{ex}}(x,T)$, in particular, for $x \geqslant 0.2$. Such a deviation has already been found in a recent comparison of $S_{\mathrm{P}}(x)$ with the low-temperature entropy $S_{\mathrm{MC}}(x,T)$ obtained by MC simulations [30]. In Fig. 4, we include $S_{\mathrm{ex}}(x,T)$ of $(Dy_{1-x}Y_x)_2Ti_2O_7$ to this comparison. For $T = 0.7$ K, $S_{\mathrm{ex}}(x,T)$ is quantitatively reproduced by $S_{\mathrm{MC}}(x,T)$ in the entire dilution range $0 \leqslant x \leqslant 0.75$. In contrast, the lowest-temperature MC data $S_{\mathrm{MC}}(x,T = 0.4\text{ K})$ overestimate the experimental results and essentially reproduce $S_{\mathrm{ex}}(x,T = 0.5\text{ K})$. Thus, an extension of the MC simulations to lower temperatures and including quantum effects would be highly desirable. Concerning the predicted nonmonotonic x dependence, a shallow maximum of the entropy around $x \approx 0.2$ is also present in $S_{\mathrm{ex}}(x,T \geqslant 0.4\text{ K})$, while below that temperature the slow thermal equilibration for $x \leqslant 0.1$ 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.

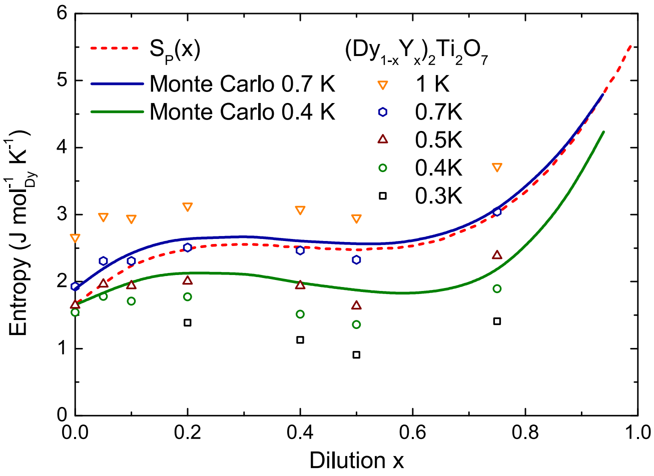

FIG. 4. (Color online) Comparison of the low-temperature entropy $S_{\mathrm{ex}}(x,T)$ of $(Dy_{1-x}Y_x)_2Ti_2O_7$ (symbols) with the corresponding $S_{\mathrm{MC}}(x,T)$ from MC simulations (solid lines [30]) and the zero-temperature residual entropy $S_{\mathrm{P}}(x)$ (dashed line) expected from a generalized Pauling approximation [29].

In conclusion, we find that the ultraslow thermal equilibration in pure spin ice $Dy_2Ti_2O_7$ is rapidly suppressed upon dilution with nonmagnetic Y and vanishes completely for $x \geqslant 0.2$. In general, the low-temperature entropy of $(Dy_{1-x}Y_x)_2Ti_2O_7$ considerably decreases with increasing x, whereas its temperature dependence drastically increases. Thus, there is no experimental evidence for a finite zero-temperature entropy in $(Dy_{1-x}Y_x)_2Ti_2O_7$ above $x \simeq 0.2$, in contrast to the finite $S_{\mathrm{P}}(x)$ expected from a generalized Pauling approximation [29]. Monte Carlo simulations of the low-temperature entropy [30] quantitatively agree with the experimental $S_{\mathrm{ex}}(x,T)$ at $T = 0.7$ K, but a systematic deviation develops at lower temperature. Thus, the classical spin-ice model is applicable down to this intermediate temperature range, but additional experimental and theoretical work is necessary to unravel the true ground state of the dilute spin ice $(Dy_{1-x}Y_x)_2Ti_2O_7$.

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