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Thermal conductivity and specific heat of the spin-ice compound $Dy_2Ti_2O_7$: Experimental evidence for monopole heat transport

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Elementary excitations in the spin-ice compound $Dy_2Ti_2O_7$ can be described as magnetic monopoles propagating independently within the pyrochlore lattice formed by magnetic Dy ions. We studied the magnetic-field dependence of the thermal conductivity $\kappa(B)$ for $B \,||\, [001]$ and observe clear evidence for magnetic heat transport originating from the monopole excitations. The magnetic contribution κ_{mag} is strongly field dependent and correlates with the magnetization $M(B)$. The diffusion coefficient obtained from the ratio of κ_{mag} and the magnetic specific heat is strongly enhanced below 1 K, indicating a high mobility of the monopole excitations in the spin-ice state.

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The recent prediction of magnetic monopoles in the spin-ice compounds has attracted a lot of interest.[1–12] Spin ice is a geometrically frustrated spin system, which is realized in $Dy_2Ti_2O_7$ by a sublattice of corner-sharing Dy^{3+} tetrahedra. Due to a strong Ising anisotropy, the magnetic moments of Dy^{3+} point either in or out of a tetrahedron. The magnetic dipole energy is minimized when two spins point in and two out of a tetrahedron (2in-2out), which is realized by 6 out of $2^4 = 16$ possible configurations for a single tetrahedron. In this respect, the spin orientation of Dy^{3+} corresponds to the hydrogen displacement in water ice[13] and the ground state is highly degenerate with a residual entropy $S_0 = Nk_B/2\ln(3/2)$ for $T \to 0$ K.[14–17] Excited states can be created by flipping one spin, resulting in two adjacent tetrahedra with configurations 3in-1out and 1in-3out, respectively. In zero magnetic field, such a dipole excitation can fractionalize into two individual excitations, a monopole (3in-1out) and an antimonopole (1in-3out), which can propagate independently. This can be visualized by flipping, e.g., another in-pointing spin of the 3in-1out tetrahedron such that it relaxes back to (another) 2in-2out ground-state configuration, while the 3in-1out state has moved to a neighboring tetrahedron.

The model of magnetic monopoles has been widely used to describe many experimental observations of $Dy_2Ti_2O_7$.[1–12] Nevertheless, there are basic properties of the spin-ice materials, which are far from being understood. For example, the specific heat c_p of $Dy_2Ti_2O_7$ has a pronounced maximum around 1.2 K resulting from the magnetic excitations, and the corresponding entropy is close to the expected $S_0 = 1.68\ \mathrm{J\,K^{-1}\,mol_{Dy}^{-1}}$.[3,16,18,19] Below ∼600 mK, however, $c_p(T)$ data published by several groups differ by almost an order of magnitude (see Fig. 1).[3,18–20] Very recently, it became clear that in this low-temperature regime, the magnetic subsystem of $Dy_2Ti_2O_7$ enters a region of very slow dynamics with relaxation processes that may extend over extremely long time scales.[11,12,19] Another open issue is the dynamics of the magnetic monopoles. The possible observation of a monopole current in an external magnetic field is currently under strong debate.[9,10,21] In this context, it is also unclear whether the magnetic monopoles contribute to the energy transport and how the monopoles interact with each other and with the phonon excitations. Suitable probes to study these issues are measurements of the thermal conductivity κ, which are the main subject of this Rapid Communication. Only one experimental study about the heat conductivity of $Dy_2Ti_2O_7$ has been published so far.[19] This previous work focuses on the anomalously enhanced relaxation times of $Dy_2Ti_2O_7$ in the low-temperature region, which are analyzed by assuming that the thermal conductivity is of purely phononic origin. In this Rapid Communication, we present a detailed study of the magnetic-field-dependent thermal conductivity $\kappa(B)$, which yields clear evidence that up to almost 50% of the low-temperature heat transport of $Dy_2Ti_2O_7$ is of magnetic origin, and our analysis suggests that this is a consequence of the high mobility of magnetic monopoles in zero field.

For the actual study, large single crystals of $Dy_2Ti_2O_7$ and $Y_2Ti_2O_7$ were grown by the floating-zone technique. The crystals were oriented in a Laue camera and samples of typical sizes of several mm^3 were cut. The thermal conductivity was measured by the standard steady-state method from ≃0.3 to 300 K. The temperature gradient was produced by a heater at one end of the sample and measured by two matched RuO_2 thermometers for $T < 15$ K in magnetic fields up to 1 T. In a separate run, the measurements were extended up to 300 K by using AuFe(0.07%)-Chromel thermocouples to detect the temperature gradient. The magnetic field was applied along [001], perpendicular to the heat current along the [110] direction of a sample of $1 \times 1 \times 3\ mm^3$ with the long edge parallel to [110]. For this sample geometry, demagnetization corrections have to be taken into account. The magnetization, needed for the correction, has been measured with a home-built Faraday magnetometer on a thin sample of $0.3 \times 2 \times 4\ mm^3$ with the long axis ‖[001] to minimize demagnetization effects.

The specific heat was measured in a home-built calorimeter using a quasiadiabatic heat-pulse method. A sample of 21 mg was fixed to the platform by a small amount of grease. The addenda were measured in a separate run and were subtracted. It has been shown recently[19] that below 600 mK, the temperature relaxation of $Dy_2Ti_2O_7$ contains multiple time constants, which can be understood if $Dy_2Ti_2O_7$ consists of subsystems weakly coupled to each other and to the platform. Standard methods to measure c_p do not account for such sample-internal dynamics, and thus provide too small values.[19] Our approach to measure c_p below 600 mK slightly differs

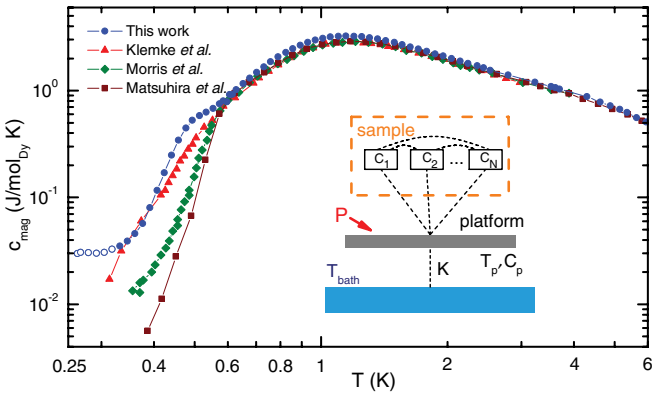

FIG. 1. (Color online) Comparison of our specific-heat data with literature data (Refs. 3,18 and 19). The low-temperature plateau of our data (open symbols) probably arises from nuclear contributions of ^{161}Dy and ^{163}Dy. Inset: Schematic illustration of the method to measure the specific heat.

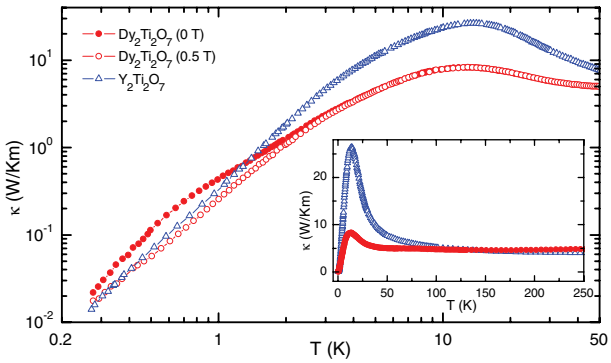

FIG. 2. (Color online) Thermal conductivity of $Dy_2Ti_2O_7$ for zero field and for 0.5 T and the zero-field thermal conductivity of the nonmagnetic $Y_2Ti_2O_7$. Inset: Same data on linear scales up to 250 K.

from that of Ref. 19. As the sample is at low temperature and in high vacuum, we can safely assume that the subsystems C_i are not directly linked to the bath, but only to each other and to the platform (inset of Fig. 1), the temperature T_P of which is measured as a function of time. Starting from equilibrium ($T_{\text{sample}} = T_P = T_{\text{bath}}$), a constant heating power P is applied to the platform until saturation is reached [$T_{\text{sample}} \simeq T_P = T_{\text{bath}} + \Delta T$ (Ref. 22)]. The heat ΔQ stored in the sample is then calculated from the total dissipated heat by subtracting the numerically obtained heat flown from the platform via K to the bath. Above 600 mK, this method yields heat capacities consistent with those obtained by conventional single-relaxation methods. At lower temperatures, however, this technique yields enhanced $c_p(T)$ data, similar to those of Ref. 19, but without any *a priori* assumptions about the subsystems or their respective couplings. Figure 1 compares our results with literature data,[3,18,19] which all agree with each other within 10% above 600 mK. For lower temperatures, however, the standard techniques[3,18] result in significantly lower c_p values than those obtained by the methods which explicitly account for the glassy behavior of different subsystems in $Dy_2Ti_2O_7$. In comparison to Ref. 19, our data show an additional shoulder in $c_p(T)$ around 500 mK and a tendency towards saturation below 350 mK. We suspect that nuclear contributions to c_p resulting from the isotopes ^{161}Dy and ^{163}Dy (Ref. 23) may, at least partly, cause the anomalous low-temperature behavior of our data, which is not observed in Ref. 19, where a ^{162}Dy-enriched sample was studied. In order to clarify the origin of these deviations, further studies on different samples are necessary. For the following discussion, this uncertainty is of minor importance, because (i) the thermal conductivity $\kappa(B)$ has only been measured above 350 mK and (ii) the deviation between our $c_p(T)$ and the data of Ref. 19 around 500 mK will affect only a single point of the diffusion coefficient discussed in the following. Nevertheless, we emphasize that due to the glassy low-temperature behavior of $Dy_2Ti_2O_7$ below 600 mK, any quantitative comparison of experimental data with theoretical models should be treated with some caution.

The thermal conductivity $\kappa(T)$ of $Dy_2Ti_2O_7$ was measured at zero and in an external magnetic field of 1 T (Fig. 2), but as mentioned above the external field was corrected by a considerable demagnetization field of up to 0.5 T. Above 4 K, there is almost no field dependence of $\kappa(T)$, while κ is significantly suppressed by a magnetic field for lower temperatures. In order to obtain information about the phononic contribution of $\kappa(T)$, we also studied the isostructural, but nonmagnetic, $Y_2Ti_2O_7$. As can be seen in the inset of Fig. 2, $\kappa(T)$ of $Dy_2Ti_2O_7$ and of $Y_2Ti_2O_7$ are very similar above 100 K, but at lower temperature $\kappa(T)$ of $Y_2Ti_2O_7$ is significantly higher than that of $Dy_2Ti_2O_7$. Probably, this difference is related to an anomaly observed at 110 K in Raman spectroscopy data that indicates a structural instability in $Dy_2Ti_2O_7$ which is absent in the nonmagnetic homologue $Lu_2Ti_2O_7$.[24,25] In addition, κ of $Dy_2Ti_2O_7$ can be reduced by phonon scattering via crystal-field excitations of the partly filled $4f$ shell of Dy. Considering the low-temperature range, it turns out that $\kappa(T)$ of $Y_2Ti_2O_7$ follows a power law $\kappa(T) \propto T^{2.4}$ below 3 K and a similar behavior [$\kappa(T) \propto T^{2.2}$] is present for the $\kappa(T)$ data of $Dy_2Ti_2O_7$ in a magnetic field of 0.5 T. In contrast, the zero-field $\kappa(T)$ of $Dy_2Ti_2O_7$ shows a clear shoulder around 1 K. This qualitative difference suggests the existence of an additional magnetic contribution κ_{mag}, which appears in the zero-field data on top of the phononic background, that is,

$$\kappa = \kappa_{\text{ph}} + \kappa_{\text{mag}}\,, \tag{1}$$

where κ_{ph} is essentially represented by the $\kappa(T)$ data measured in 0.5 T. This conclusion is confirmed by measurements of the field-dependent $\kappa(B)$ at constant temperatures. Again, demagnetization has been taken into account to rescale the magnetic field. Figure 3 displays the relative change κ/κ_0 for different constant temperatures. Below 2 K, we find a steplike decrease of $\kappa(B)$ around 0.2 T, which systematically sharpens on decreasing temperature. As is shown exemplarily for 800 mK in Fig. 3(a), this step is followed by a weak, essentially linear decrease towards higher fields. The relative reduction κ/κ_0 has a maximum around 600 mK and vanishes practically above 4 K. The decrease of $\kappa(B)$ correlates with the increase of $M(B)$, shown exemplarily for 700 and 500 mK in Figs. 3(b) and 3(d), respectively. The steplike change of κ/κ_0 exhibits a clear hysteresis below 700 mK [Figs. 3(c)–3(e)], with different critical fields depending on the field-sweep direction.

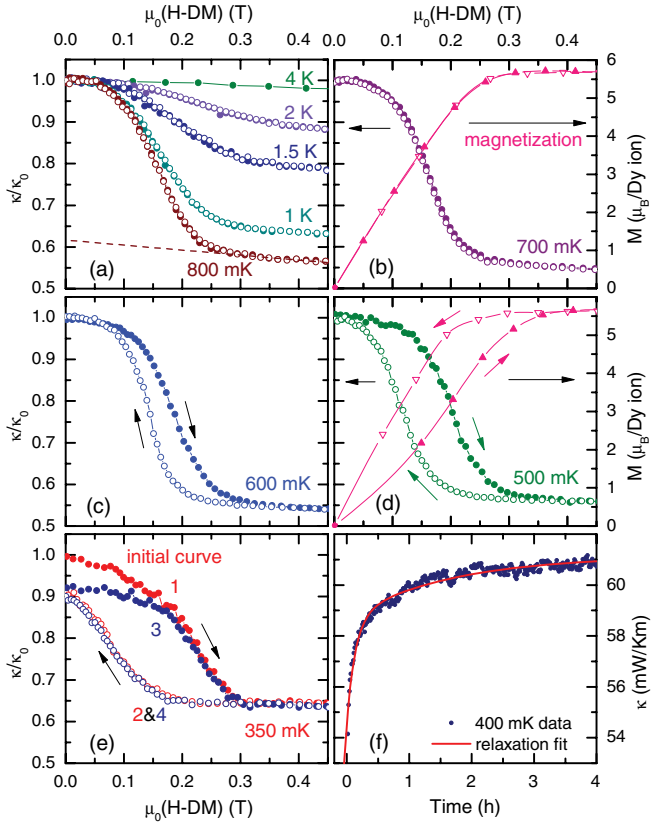

FIG. 3. (Color online) Field dependence of $\kappa(B)/\kappa(0\,\mathrm{T})$ for $B\,||\,[001]$. All curves were measured after zero-field cooling. The fit of the linear decrease above ∼0.3 T is shown exemplarily for 800 mK. Panels (b) and (d) also contain the magnetization data $M(B)$ (△), and (f) displays the time-dependent relaxation $\kappa(0\,\mathrm{T},t)$ back to the initial zero-field value for 400 mK.

Finally, an additional feature appears in $\kappa(B)$ below 500 mK [Fig. 3(e)]: Measuring an initial curve (1) after zero-field cooling and subsequently decreasing the magnetic field back to zero (curve 2), $\kappa(0\,\mathrm{T})$ only recovers about 90% of its original zero-field value. Repeating the field sweeps from this new starting point results in $\kappa(B)$ curves (3) and (4) with coinciding endpoints, where curves (2) and (4) perfectly match each other. The reduced zero-field values $\kappa(0\,\mathrm{T})$ slowly relax back to the respective zero-field-cooled values, as is shown in Fig. 3(f) for 400 mK. In order to describe this relaxation process, at least two relaxation times are needed, that is,

$$\kappa(t) = a_0 + a_1(1 - e^{-t/\tau_1}) + a_2(1 - e^{-t/\tau_2}). \qquad (2)$$

The fit of Fig. 3(f) yields large relaxation times $\tau_1 \simeq 8$ min and $\tau_2 \simeq 100$ min. As every data point of $\kappa(B)$ in Figs. 3(a)–3(e) requires several minutes of temperature stabilization, the different zero-field values [Fig. 3(e)] originate from the extremely slow relaxation τ_2.[26] This very slow relaxation only occurs after a field sweep below 500 mK but not after cooling at zero field. Such a slow glasslike low-temperature behavior of $Dy_2Ti_2O_7$ is in agreement with various recent papers.[6,19,27,28]

A straightforward qualitative interpretation of the observed magnetic-field dependent $\kappa(B)$ is obtained by assuming that the magnetic contribution κ_{mag} results from a heat transport by magnetic monopoles. Due to the degenerate zero-field

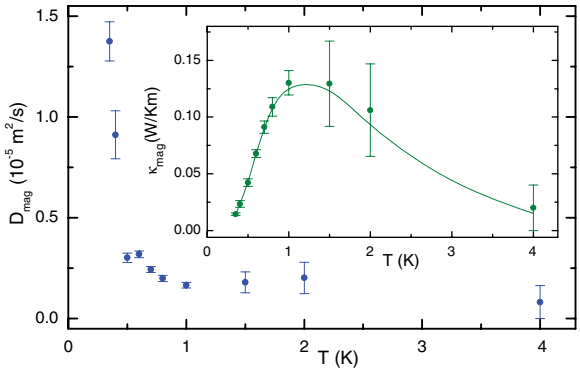

FIG. 4. (Color online) Magnetic contribution κ_{mag} of the zero-field heat transport (inset; the line is to guide the eye) and the diffusion coefficient $D_{\mathrm{mag}} = \kappa_{\mathrm{mag}}/c_{\mathrm{mag}}$.

ground state (2in-2out), a monopole excitation (3in-1out or 1in-3out) can easily propagate by single spin flips. When a monopole excitation passes through a 2in-2out tetrahedron, two subsequent single spin flips are needed, which change the initial 2in-2out configuration of this tetrahedron to another 2in-2out state. Because in zero magnetic field all 2in-2out configurations are degenerate the magnetic monopoles have a large mobility. In other words, the monopoles and antimonopoles are not confined to each other in zero magnetic field. This drastically changes in a magnetic field along [001], which lifts the ground-state degeneracy. As a consequence, the monopoles get more and more confined by increasing the tension of the Dirac strings connecting the monopole/antimonopole pairs. Thus, with increasing field, the (independent) monopole mobility decreases on the one hand, while the energetic preference of one particular 2in-2out configuration is reflected by the increasing magnetization $M(B)$ on the other hand, which explains the observed correlation between increasing magnetization and decreasing heat conductivity (see Fig. 3). With increasing $B||[001]$, the monopole excitation energy also increases weakly, i.e., the monopole density decreases, but we expect this effect to be of minor importance because the decreasing monopole mobility due to the field-induced lifting of the ground-state degeneracy will be the dominating effect. For magnetic fields above the steplike decrease of $\kappa(B)$, the heat transport is purely phononic, and in order to extract the zero-field phononic contribution, we extrapolate the weak linear decrease of $\kappa(B)$ back to 0 T [Fig. 3(a)]. The extrapolation uncertainties determine the error bars of κ_{mag}. The resulting zero-field magnetic contribution κ_{mag} has a pronounced maximum at ∼1.2 K (inset of Fig. 4). The maximum of κ_{mag} is located close to that of c_{mag}, but on further increasing temperature κ_{mag} rapidly decreases and practically vanishes above ∼4 K. In Ref. 19, the zero field $\kappa(T)$ of $Dy_2Ti_2O_7$ was assumed to be purely phononic and its field dependence has been attributed to phonon scattering by magnetic excitations. Our data do not, however, support this interpretation. First of all, the phonon heat conductivity $\kappa(T)$ of the nonmagnetic reference compound $Y_2Ti_2O_7$ shows a very similar power-law behavior as the thermal conductivity of $Dy_2Ti_2O_7$ in a field of 0.5 T. Second, the anticorrelation of $\kappa(B)$ and $M(B)$ is explained straightforwardly by the monopole

confinement due to an external magnetic field. Thus, our data give evidence for an additional magnetic contribution κ_{mag} in zero magnetic field arising from the monopole excitations of $Dy_2Ti_2O_7$. The corresponding diffusion coefficient

$$D_{\mathrm{mag}} = \frac{\kappa_{\mathrm{mag}}}{c_{\mathrm{mag}}} \tag{3}$$

is displayed in the main panel of Fig. 4. Above 1 K, D_{mag} is almost temperature independent, but strongly increases towards lower temperatures. This fits to the qualitative expectation of a high monopole mobility by single spin flips on the degenerate ground state. At low temperatures, the monopole excitations are highly dilute, resulting in a large mean-free path and hence a large diffusion coefficient. With increasing temperature, the number of monopoles increases and thus the diffusion coefficient is expected to decrease. In the simplified model of single spin flips, this follows from the fact that a monopole can pass an already excited tetrahedron, i.e., another (anti)monopole, only via simultaneous spin flips. Within kinetic gas theory, the diffusion coefficient is related via $D = v\ell/3$ with the mean velocity v and the mean-free path ℓ of the particles, but this relation can not be directly applied to the actual monopole gas in $Dy_2Ti_2O_7$ for various reasons. First of all, the number of monopoles is not conserved and, moreover, neither the (average) velocity of monopoles nor their interaction with each other or with the phonon excitations is well understood up to now. Quite recently, an expression for the monopole mobility in a (magnetic or electric) field has been derived,[5] but it is unclear whether this result can be related to our experimental D_{mag} arising from a finite-temperature gradient in zero field. Despite these uncertainties, we give a rough estimate of a mean-free path by assuming the monopole velocity to be $v = t_{\mathrm{eff}}/(\hbar\pi/a_d) \sim 20$ m/s, which results from the distance of neighboring tetrahedra $a_d = 4.34$ Å and assuming an effective bandwidth for monopole hopping t_{eff} of the order of 1 K. The mean-free path $\ell = 3D_{\mathrm{mag}}/v$ linearly scales with $D_{\mathrm{mag}}(T)$ and reaches the μm range, i.e., $\sim$1000 unit cells for $T < 700$ mK, which may be understood from the low monopole density. Moreover, we can estimate the scattering time $\tau = \ell/v$ to be in the μs range, in agreement with relaxation times observed by muon spin rotation.[9,29] However, even around $\sim$2 K, ℓ is still of the order of $\sim$100 unit cells although the mean monopole distance is of the order of a_d. This suggests that at least towards higher temperatures, more complex hopping models have to be involved to describe $\kappa_{\mathrm{mag}}(T)$.

In conclusion, we observe clear evidence for a considerable magnetic contribution κ_{mag} to the heat transport in the spin-ice material $Dy_2Ti_2O_7$. At constant temperature, the magnetic-field-dependent decrease of $\kappa(B)$ correlates with the increase of the magnetization $M(B)$ and thus with the lifting of the ground-state degeneracy. This reveals that the complete suppression of κ_{mag} in a magnetic field of about 0.5 T arises from the loss of monopole mobility or, vice versa, the large $\kappa_{\mathrm{mag}}(0\,\mathrm{T})$ is a consequence of the zero-field ground-state degeneracy. Including specific-heat data, we derive a strong increase of the diffusion coefficient below 1 K, which is most probably related to the fact that the monopole gas is highly dilute towards low temperature. In order to derive quantitative information about, e.g., the mean-free path or the velocities, theoretical models about the monopole dynamics are required.

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