The recent prediction of magnetic monopoles in the spin-ice compounds has attracted a lot of interest \[1\]–\[4\]. Spin ice is a geometrically frustrated spin system, which is realized in Dy$_2$Ti$_2$O$_7$ 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. The magnetic dipole energy is minimized, when two spins point in and two out of a tetrahedron (2in-2out), what is realized by 6 out of 24 = 16 possible configurations for a single tetrahedron. In this respect, the spin orientation of Dy$^{3+}$ corresponds to the hydrogen displacement in water ice \[11\] and the ground state is highly degenerate with a residual entropy $S_0 = Nk_B/2 \ln(3/2)$ for $T \to 0$ K \[12\].\[13\]. 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 anti-monopole (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$_2$Ti$_2$O$_7$ \[14\]–\[10\]. 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$_2$Ti$_2$O$_7$ has a pronounced maximum around 1.2 K resulting from the magnetic excitations and the corresponding entropy is close to the expected $S_0 = 1.68$ J K$^{-1}$ mol$_{Dy}^{-1}$ \[2\]–\[4\],\[14\]–\[17\]. Below ~600 mK, however, $c_p(T)$ data published by several groups differ by almost an order of magnitude, see figure \[14\]–\[16\],\[17\]. Very recently it became clear that in this low-temperature regime the magnetic subsystem of Dy$_2$Ti$_2$O$_7$ enters a region of very slow dynamics with relaxation processes that may extend over extremely long time scales \[15\]–\[17\]. 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 \[1\]–\[3\],\[14\]–\[19\]. 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. A suitable probe to study these issues are measurements of the thermal conductivity $\kappa$, which are the main subject of this report. Only one experimental study about the heat conductivity of Dy$_2$Ti$_2$O$_7$ has been published so far \[17\]. This previous work focuses on the anomalously enhanced relaxation times of Dy$_2$Ti$_2$O$_7$ in the low-temperature region, which are analyed by assuming that the thermal conductivity is of purely phononic origin. In this report, 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$_2$Ti$_2$O$_7$ 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$_2$Ti$_2$O$_7$ and Y$_2$Ti$_2$O$_7$ 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 $\parallel$[001] to
minimize demagnetization effects.

The specific heat was measured in a home-built calorimeter using a quasi-adiabatic heat-pulse method. A sample of 21 mg was fixed to the platform by a small amount of grease. The addenda was measured in a separate run and was subtracted. It has been shown recently [17], that below 600 mK the temperature relaxation of Dy$_2$Ti$_2$O$_7$ contains multiple time constants, which can be understood by Dy$_2$Ti$_2$O$_7$ consisting 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 [17]. Our approach to measure $c_p$ below 600 mK, slightly differs from that of [17]. 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 figure 1), whose temperature $T_p$ 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 ($T_{\text{sample}} \approx T_p = T_{\text{bath}} + \Delta T$ [20]). The heat $\Delta Q$ 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 [17], but without any a-priori assumptions about the subsystems or their respective couplings. Figure 1 compares our results with literature data [2, 16, 17], which all agree with each other within 10% above 600 mK. For lower temperatures, however, the standard techniques [2, 16] 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$_2$Ti$_2$O$_7$. In comparison to [17], 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 [21] may, at least partly, cause the anomalous low-temperature behavior of our data, which is not observed in [17], 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 [17] around 500 mK will affect only a single point of the diffusion coefficient discussed below.

Nevertheless, we emphasize that due to the glassy low-temperature behavior of Dy$_2$Ti$_2$O$_7$ 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$_2$Ti$_2$O$_7$ was measured at zero and in an external magnetic field of 1 T (figure 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 $\kappa$ 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 iso-structural, but non-magnetic Y$_2$Ti$_2$O$_7$. As can be seen in the inset of figure 2 $\kappa(T)$ of Dy$_2$Ti$_2$O$_7$ and of Y$_2$Ti$_2$O$_7$ are very similar above 100 K, but at lower temperature $\kappa(T)$ of Y$_2$Ti$_2$O$_7$ is significantly higher than that of Dy$_2$Ti$_2$O$_7$. Probably, this difference is related to an anomaly observed at 110 K in Raman spectroscopy data that indicates a structural instability in Dy$_2$Ti$_2$O$_7$ which is absent in the non-magnetic homologue Lu$_2$Ti$_2$O$_7$ [22, 23]. In addition, $\kappa$ of Dy$_2$Ti$_2$O$_7$ 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$_2$Ti$_2$O$_7$ 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

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**FIG. 1.** (color online). Comparison of our specific heat data with literature data [2, 16, 17]. 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$_2$Ti$_2$O$_7$ for zero field and for 0.5 T and the zero-field thermal conductivity of the non-magnetic Y$_2$Ti$_2$O$_7$. Inset: Same data on linear scales up to 250 K.
\( \kappa(T) \) data of Dy₂Ti₂O₇ in a magnetic field of 0.5 T. In contrast, the zero-field \( \kappa(T) \) of Dy₂Ti₂O₇ shows a clear shoulder around 1 K. This qualitative difference suggests the existence of an additional magnetic contribution \( \kappa_{\text{mag}} \), which appears in the zero-field data on top of the phononic background, that is

\[
\kappa = \kappa_{\text{ph}} + \kappa_{\text{mag}},
\]

where \( \kappa_{\text{ph}} \) 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 3a displays the relative change \( \kappa/\kappa_0 \) for different constant temperatures. Below 2 K, we find a step-like decrease of \( \kappa/\kappa_0 \) 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 mK and 500 mK in figure 3b and 3c, respectively. The step-like decrease of \( \kappa/\kappa_0 \) exhibits a clear hysteresis below 700 mK (figure 3b-c), with different critical fields depending on the field-sweep direction.

Finally, an additional feature appears in \( \kappa(B) \) below 500 mK (figure 3c): Measuring an initial curve (1) after zero-field cooling and subsequently decreasing the magnetic field back to zero (curve 2), \( \kappa(0 \text{T}) \) 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 \( \kappa(0 \text{T}) \) slowly relax back to the respective zero-field-cooled values, as is shown in Figure 3 for 400 mK. In order to describe this relaxation process at least two relaxation times are needed, that is

\[
k(t) = a_0 + a_1(1 - e^{-t/\tau_1}) + a_2(1 - e^{-t/\tau_2}).
\]

The fit of figure 3 yields large relaxation times \( \tau_1 \approx 8 \text{ min} \) and \( \tau_2 \approx 100 \text{ min} \). As every data point of \( \kappa(B) \) in figure 3-a requires several minutes of temperature stabilization, the different zero-field values (figure 3-b) originate from the extremely slow relaxation \( \tau_2 \). This very slow relaxation only occurs after a field sweep below 500 mK but not after cooling at zero field. Such a slow glass-like low-temperature behavior of Dy₂Ti₂O₇ is in agreement with various recent reports [3, 17, 25, 26].

A straightforward qualitative interpretation of the observed magnetic-field dependent \( \kappa(B) \) is obtained by assuming that the magnetic contribution \( \kappa_{\text{mag}} \) results from a heat transport by magnetic monopoles. Due to the degenerate zero-field 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. As in zero magnetic field all 2in-2out configurations are degenerate, the magnetic monopoles have a large mobility. This drastically changes in a magnetic field along [001], which lifts the degeneracy of the different 2in-2out configurations and thus the monopole mobility is suppressed. In addition, the correlation between increasing magnetization and decreasing heat conductivity is explained. The magnetic field determines, which 2in-2out state is the field-induced ground state, and for not too small fields (\( \geq 0.1 \text{T} \)), the magnetization is proportional to the population of this particular 2in-2out state, whereas the monopole mobility systematically decreases the more this 2in-2out state is populated. 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 step-like 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 (figure 3a). The extrapolation uncertainties determine the error bars of \( \kappa_{\text{mag}} \). The resulting zero-field magnetic contribution \( \kappa_{\text{mag}} \) has a pronounced maximum at \( \sim 1.2 \) K (inset of figure 3). The maximum of \( \kappa_{\text{mag}} \) is located close to that of \( c_{\text{mag}} \), but on further increasing temperature \( \kappa_{\text{mag}} \) rapidly decreases and practically vanishes above \( \sim 4 \) K. The main panel of figure 4 displays the corresponding diffusion coefficient,

\[
D_{\text{mag}} = \frac{\kappa_{\text{mag}}}{c_{\text{mag}}},
\]

Above 1 K, \( D_{\text{mag}} \) 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 \( \ell \) of the particles, but this relation cannot be directly applied to the actual monopole gas in Dy\(_2\)Ti\(_2\)O\(_7\) 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 [4], but it is unclear whether this result can be related to our experimental \( D_{\text{mag}} \) arising from a finite temperature gradient in zero field. Despite these uncertainties, we give a rough estimate of a mean-free path by assuming a monopole velocity \( v = a_d v \approx 20 \text{ m/s} \). Here, \( a_d = 4.34 \text{ Å} \) denotes the distance of neighboring tetrahedra and \( v \) is the rate of single spin flips, which we roughly estimate by the monopole excitation energy \( E_m \approx 2.2 \text{ K} \) [3] to \( v = E_m / h = 4.6 \times 10^{10} \text{ s}^{-1} \). Assuming a temperature-independent \( v \), \( \ell = 3D_{\text{mag}} / v \) yields a linear scaling from \( D_{\text{mag}}(T) \) to \( \ell(T) \). As shown in figure 1 (right scale), within this estimate \( \ell(T) \) reaches the \( \mu \text{m} \) range, i.e. \( \sim 1000 \) unit cells, for \( T < 500 \text{ mK} \), which may be understood from the low monopole density. However, even around \( \sim 2 \) K, \( \ell \) is still of the order \( \sim 100 \) unit cells although almost every second tetrahedron is in an excited 3in-1out or 1in-3out configuration. This suggests that at least towards higher temperatures, more complex hopping models have to be involved to describe \( \kappa_{\text{mag}}(T) \).

In conclusion, we observe clear evidence for a considerable magnetic contribution \( \kappa_{\text{mag}} \) to the heat transport in the spin-ice material Dy\(_2\)Ti\(_2\)O\(_7\). At constant temperature, the magnetic-field dependent decrease of \( \kappa(B) \) correlates with the increase of the magnetization \( M(B) \), which measures the population of the particular 2in-2out configuration becoming the field-induced non-degenerate ground state. This reveals that the complete suppression of \( \kappa_{\text{mag}} \) in a magnetic field of about 0.5 T arises from the loss of monopole mobility or, vice versa, the large \( \kappa_{\text{mag}}(0 \text{ T}) \) is a consequence of the zero-field ground state degeneracy. Our data also reveal a strong increase of the relaxation times below about 600 mK. 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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and in order to avoid systematic errors induced by time-dependent experimental conditions, the heating curves $T_P(t)$ have to be cut off after suitable times, typically 5 – 10 minutes. Further relaxation can be estimated to increase $c_p$ by only a few percent. Thus, the presented data represent lower bounds for $c_p$.  

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