Enhanced thermal Hall conductivity below 1 Kelvin in the pyrochlore magnet Yb$_2$Ti$_2$O$_7$

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Abstract

Clean samples of $R_2$Ti$_2$O$_7$ with $R$=Yb have a sharp first-order transition to canted ferromagnetic (C-FM) order at $T_C = 0.275$ K. However, at temperature $T > T_C$, a correlated paramagnetic state may show hallmarks of strong correlations. In this letter, we report a study of the magnetic heat carriers in Yb$_2$Ti$_2$O$_7$ by means of the thermal Hall conductivity $\kappa_{xy}$, the transverse element of the full thermal transport tensor $\kappa_{ij}$. The thermal Hall conductivity has two contributions of opposite sign: At the lowest $T$ and high magnetic field $H$, negative $\kappa_{xy}$ is the characteristic feature of magnons in the collinear field-aligned ferromagnetic (FA-FM) state. This magnon Hall signal is suppressed with $H$ when a Zeeman gap opens. In contrast, the paramagnetic state (PM) is endowed with a very large positive $\kappa_{xy}$, which onsets at $T \sim 3$ K and persists in weakened form even at $T < T_C$. We ascribe this signal to unconventional quasiparticles with spin gap $< 40 \mu$eV in the correlated paramagnetic state of this frustrated magnet. By comparing the thermal conductivities $\kappa_{xx}$ for $R$=Tb, Yb, and Y, we are able to rule out a phonon skew
scattering scenario for $\kappa_{xy}$. Our result represents the first positive report of a thermal Hall signal measured in a dilution refrigerator ($T < 0.290$ K).

**Main Text:**

Rare earth pyrochlore titanates $R_2\text{Ti}_2\text{O}_7$ have served as a playground for the study of geometrically frustrated magnetic interactions for more than two decades [1]. For $R$=Dy, Ho, strong crystal field effects constrain the rare earth moments to be fully aligned with the *local* Ising axis (Fig. 1a). Such a pyrochlore lattice with ferromagnetic interactions and local easy axis can be mapped onto an Ising model on the diamond lattice with antiferromagnetic interactions and global easy axis [2], a system with macroscopic ground state degeneracy [3]. This is the celebrated 'classical spin-ice' state, where moments on each tetrahedron follow a two-in-two-out rule and spin-flip excitations can be interpreted as effective monopoles [4].

For theorists, a popular perturbative approach is to introduce quantum fluctuations by continuously weakening the strength of the local Ising anisotropy. If transverse fluctuations of the magnetic moments are strong enough, they are expected to lead to a 'melting' of the spin-ice state [5]. This line of thought has led to enhanced interest in two titanate compounds: Tb$_2$Ti$_2$O$_7$ with large $^7F_6$ moments has moderate local Ising anisotropy on the single-ion level and dominant antiferromagnetic interactions [6][7], while Yb$_2$Ti$_2$O$_7$ with small $^2F_{7/2}$ moments is a single-ion XY system with ferromagnetic interactions [8][9].
It has been argued that the introduction of spin-orbit coupling and dipolar interactions, in addition to Heisenberg exchange and local ion anisotropy, may renormalize the effective Hamiltonian ($R$=Yb, [10]) or even change the sign of the dominant interaction ($R$=Tb) [1]. Thus, a spin-ice model with enhanced quantum fluctuations may be the appropriate model to describe the low-energy behavior of both materials. Experimental support for ice-like correlations comes from observations of pinch-points in diffuse elastic neutron scattering in the paramagnetic state of $R$=Yb, Tb [11][12]. Furthermore, such correlations are also evident in the likely two-in-two-out canting of the C-FM state in $R$=Yb [13]. However, the nature of the dominant interaction in $R$=Yb,Tb remains a matter of contentious debate [14].

What are the advantages of working with $R$=Yb? Although our study reveals similarities of the thermal transport in the PM state of $R$=Yb,Tb, $\text{Yb}_2\text{Ti}_2\text{O}_7$ is distinguished by its simple crystal electric field (CEF) level scheme for the magnetic ion: While a low-lying third CEF state is located only $\varepsilon_1=15$ K above the ground state in $R$=Tb [6], such a state is absent in $R$=Yb, where $\varepsilon_1>800$ K [8]. This makes the present system more amenable to theoretical modeling. The Kramers nature of the Yb$^{3+}$ ion is also expected to suppress skew scattering of phonons. Furthermore, the Hamiltonian parameters are in principle well known from high-resolution studies of inelastic neutron scattering in a magnetic field [10][14]. And, fourth and finally, single crystals of the highest quality are now available for $\text{Yb}_2\text{Ti}_2\text{O}_7$.

Careful recent work on the chemical properties of rare earth titanates has revealed that slight stuffing $R_{2+x}\text{Ti}_{2-x}\text{O}_{7+\delta}$ with $x=0.01$-$0.04$ is common for single crystals of $R$=Tb,
Yb grown by the optical float zone technique [9][15][16]. Both stoichiometric compounds were shown to host complex magnetic order, which is suppressed in the stuffed derivatives despite the low dopant concentration. For $R=$Yb, these results motivated growth of the large, high-purity single crystals with $|x|<0.005$ used in this study using an advanced traveling-solvent floating zone technique [9].

Thermal conductivity $\kappa_{xx}$ and the thermal Hall effect $\kappa_{xy}$ are experimental tools which open a window on the propagating low-energy quasiparticles of a magnetic insulator. Previous experimental work has confirmed the existence of a finite $\kappa_{xy}$ in ferromagnetic insulators with certain crystal structures, despite the absence of a Lorentz force acting on the heat carriers [17] [18]. The theoretical underpinning is provided by calculations based on the Berry phase formalism [19] [20]. In addition to a wealth of theoretical predictions of $\kappa_{xy}$ in various insulating long-ranged ordered magnets, the focus of recent experimental research has moved towards frustrated magnets, their exotic elementary excitations, and associated thermal Hall responses [21] [22].

We employ a standard experimental technique with one heater and three thermometers attached to a thin, rectangular plate of single crystalline sample standing free in vacuum (see Supplementary Information [23]). The sample was cooled with the help of a He-3 cryostat or a dilution refrigerator. We apply the heat current $J_{Q}/\langle 110 \rangle$. This work focuses on the configuration $H/\langle 111 \rangle$, both in order to facilitate comparison with earlier scattering experiments, and because the crystal structure of the pyrochlore lattice takes a particularly simple form in this configuration [23].
From the raw data of $\kappa_{xy}/T$ (entropy factor removed), two major regimes of the phase diagram can be distinguished (Fig. 1c): At low $T$ and high $H$, negative $\kappa_{xy}/T$ is observed in the collinear field-aligned ferromagnetic (FA-FM) ground state, which was previously reported in neutron scattering and magnetization measurements [13]. The Hall signal is exponentially suppressed in very large $H$, when the Zeeman gap $\Delta Z$ in the spin spectrum grows larger than $k_B T$. Independently, at high $T$ and low $H$, enhanced positive $\kappa_{xy}/T$ appears in the correlated paramagnetic (PM) state. Finite positive $\kappa_{xy}/T$ persists, in weakened form, even into the long-range ordered phase at $T<T_C$.

Before advancing to a semi-quantitative analysis of the thermal Hall signal in Yb$_2$Ti$_2$O$_7$, a discussion of phonon skew scattering from magnetic ions in rare earth pyrochlore titanates appears necessary. In the past, this mechanism has been proposed as a possible origin of finite $\kappa_{xy}$ in insulators [24]. We compare thermal transport in $R=Yb$ (Kramers ion Yb$^{3+}$) and $R=Tb$ (non-Kramers ion Tb$^{3+}$) with the aim of ruling out the phonon scattering scenario for $\kappa_{xy}$ (Fig. 2a). In this figure, it is apparent that $\kappa_{xx}$ in $R=Tb$ is suppressed by an order of magnitude as compared to $R=Yb$, $Y$ at low $T$. In fact, a very short phonon mean free path of $\sim 1 \mu$m was derived from comparable $\kappa_{xx}$ data for $R=Tb$ in Ref. [25]. Inelastic neutron scattering experiments provide additional evidence for strong spin-phonon coupling in Tb$_2$Ti$_2$O$_7$, revealing directly a split of the nearly degenerate ground state crystal electric field (CEF) doublet [26]. This split is allowed due to the non-Kramers nature of the Tb$^{3+}$ shell, while only magnetic exchange (i.e. local time-reversal symmetry breaking) may split the CEF ground state doublet in the Kramers ion Yb$^{3+}$. 
Despite the reduced phonon scattering in $R=Yb$, its $\kappa_{xy}$ signal is comparable to or larger than the one in $R=Tb$ [23]. This is qualitatively inconsistent with the phonon skew scattering scenario. Instead, we propose that the $\kappa_{xy}$ signal reported in this manuscript is entirely due to magnetic excitations.

We focus first on $\kappa_{xy}$ in the FA-FM state of $R=Yb$, where magnon quasiparticles have been studied extensively in inelastic neutron scattering and THz experiments [10][14][27]. The basis of our analysis is the analytical expression for the thermal Hall effect due to Berry curvature of the magnon bands,

$$\kappa_{xy} = -\frac{\kappa_B T}{h\nu} \sum_{nk} \Omega_n z_\nu(k) c_2(\rho_B(\epsilon_{nk}))$$ (1)

where the summation is executed over all quasiparticle bands $n$ and momentum space states $k$, $\Omega_n z$ is the component of the Berry curvature vector parallel to the global magnetization, $\rho_B$ is the Bose-Einstein distribution function, $\epsilon_{nk}$ are quasiparticle energies, and $c_2(\rho_B)$ is a nonlinear, but monotonically decreasing function [20]. It is believed that this formalism is applicable to all systems of non-interacting quasiparticles, if $\rho_B$ is replaced by the appropriate distribution function. We emphasize that Eq. (1) for $\kappa_{xy}$ is explicitly independent of the mean free path of heat carriers, similar to the case of the intrinsic anomalous Hall conductivity in conducting systems with non-trivial band structures [28][29].

If an effective Berry curvature $\tilde{\Omega}$ can be assigned to all states populated at low $T$ independent of $n$ and $k$, the temperature dependence of $\kappa_{xy}$ is dominated by changes in the number density of heat carrying excitations, so that
\[ \kappa_{xy}/T = (\kappa_{xy}/T) \cdot \exp(-\beta \Delta) \equiv (\kappa_{xy}^0/T) \cdot \exp(-\beta \Delta) \quad (2) \]

and the total spin gap is a combination of Zeeman (field dependent) and anisotropy (field independent) contributions viz. \[ \Delta = \Delta_A + \Delta_Z = \Delta_A + g \mu_B \mu_0 H. \] Here, \( \mu_B \) is the Bohr magneton, \( \beta = (k_B T)^{-1} \), and we have introduced an effective \( g \)-factor.

We test Eq. (2) using a scaling analysis in the FA-FM state (Fig. 3c), where all the curves of \( \ln(\kappa_{xy}/T) \) are found to collapse onto a universal line as a function of \( \beta \Delta_Z \sim \beta \mu_0 H \), if a field-independent term \( \sim \beta \Delta_A \) is subtracted. This yields an effective \( g = 1.4 \), reasonably close to the \( g=2 \) expected for pseudospin-1/2 Yb\(^{3+} \) moments. Fitting the field-independent term \( \ln(\kappa_{xy}^0/T) \) as a function of \( T \), we also obtain the anisotropy gap in the FA-FM state: \( \Delta_A = 78 \mu \text{eV} \) (Fig. 3C). Note that \( \Delta_A \) in the FA-FM state is not necessarily identical to the \( \Delta_A \) of the C-FM state at low \( H \). A similar scaling analysis, albeit for \( \kappa_{xx} \), was successful in establishing the magnon contribution to thermal transport in the Kagome ferromagnet Cu(1,3-bdc) [18].

Finally turning our attention to the PM regime, first recall that the nature of low-lying excitations in the PM and C-FM states of \( R=Yb \) is a matter of some debate. For example, recent quasi-elastic and inelastic neutron scattering just above \( T_C \) suggest an excitation spectrum with a vanishing or very small (\( \sim \mu \text{eV} \)) spin gap [30]. Meanwhile, thermal conductivity \( \kappa_{xx}(H) \) measurements have reported heat carriers with a substantial excitation gap (\( \sim 170 \mu \text{eV} \)) [31]. We address this issue through the low-field slope of the thermal Hall conductivity \( [\kappa_{xy}/(TB_{\text{ext}})]_0 = [\kappa_{xy}/(TB_{\text{ext}})]_{H \rightarrow 0} \) (Fig. 4), where \( B_{\text{ext}} = \mu_0 H \). In this limit of linear response, the onset of a finite \( \kappa_{xy} \) is observed just below \( T = 3 \) K. This is in good agreement with a hump in the specific heat \( c_P(T) \) around the same \( T \) [32],
which is usually associated with the energy scale of the dominant nearest-neighbor interaction $J$ in this material [33]. As $T$ is lowered further, $[\kappa_{xy} / (TB)]_0$ increases sharply below 0.5 K, deviating from a smooth $T$-dependence. Following a maximum of $[\kappa_{xy} / (TB_{\text{ext}})]_0$ around $T=0.35$ K, the signal finally starts to decrease continuously as $T_c = 0.265$ K is approached and transgressed. We compare $\kappa_{xy}$ to specific heat data for a comparable sample (Fig. 4c, adapted from [9]). The presence of a maximum in $[\kappa_{xy} / (TB_{\text{ext}})]_0$ at $T = 0.4$ K strongly suggests that the spin gap of the PM state should be smaller than 40 $\mu$eV.

The enhancement of $[\kappa_{xy} / (TB_{\text{ext}})]_0$ in the regime above $T_c$ reported here was foreshadowed in a combined study of elastic neutron scattering, heat capacity, and magnetization measurements by Scheie et al. [13]. These authors reported that the critical temperature $T_c$ of the C-FM state of Yb$_2$Ti$_2$O$_7$ increases with a small $H //<111>$, resulting in an unconventional lobe-shaped phase diagram (reproduced in Fig. 1c, open symbols). This was taken as evidence for strong fluctuations in the PM state preempting the transition to long range order. The applied field can suppress these fluctuations, and thus increase $T_c$ [13]. In our data, the largest fluctuation-Hall signal characterizing the PM state is observed in the range of 0.3-0.5 K, the regime identified by Ref. [13] to be dominated by quantum fluctuations.

We expect that future high-resolution neutron scattering and other microscopic probes can give more insight into the nature of the correlated PM state in $R=Yb, Tb$. Our work has revealed that this state hosts heat carriers with an unconventional coupling to the external magnetic field, resulting in a transverse effective force even for charge-
neutral quasiparticles. As far as the collinear FA-FM state, induced by a magnetic field, is concerned, a quantitative calculation based on Eq. (1), starting from the magnon band structure observed in inelastic neutron scattering [14], is expected to reproduce our transport results.

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Figure 1: (a) Illustration of the pyrochlore crystal structure. Only the rare-earth sublattice is shown (blue dots); it forms a network of corner-sharing tetrahedra. A pair of rare-earth tetrahedra detailed in (b) is highlighted in red color. (Real space) crystallographic directions are indicated with arrows. (b) The crystal fields at each rare earth site (blue) are dominated by the surrounding oxygen ions (red). Transition metal ions are not shown. Direction of local <111> direction for central rare earth ion is indicated. (c) Contour plot of thermal Hall conductivity $\kappa_{xy}/T$ distinguishes the correlated high-$T$ paramagnetic (PM)
state with a large positive $\kappa_{xy}$ from the low-$T$, high-$H$ collinear field-aligned ferromagnetic (FA-FM) regime with a weak negative $\kappa_{xy}$. The black circles mark the phase transition to canted ferromagnetic (C-FM) order taken from [13]. The positive $\kappa_{xy}$ signal persists into the C-FM state. (e-f): Field dependence of $\kappa_{xy}/T$ at various $T$. The alignment of the magnetic field was $H // <111>$, and the heat current was $J_Q // <110>$.
Figure 2: (a) Comparison of zero-field thermal conductivity $\kappa_{xx}$ for various $R_2\text{Ti}_2\text{O}_7$ compounds. At high $T \sim 20$ K, the large maximum of $\kappa_{xx}$ in $R=$Yb indicates excellent sample quality. Phonon scattering at low $T$ is strongest in $R=$Tb (from Ref. [21]), and weakest in non-magnetic $R=$Y (from Ref. [25]). (b) Low-$T \kappa_{xx}/T$ for $R=$Yb, showing a kink in the curve at the phase transition to C-FM order at $T_C = 0.265$ K. The black line is a guide to the eye.
Figure 3: Scaling analysis of $\kappa_{xy}$ in the FA-FM state. (a) Starting from the raw data of the thermal Hall conductivity $\kappa_{xy}/T$, we focus on the negative signal observed above $\mu_0 H = 1$ T (red box). (b) According to Eq. (2), we expect linear dependence of $\ln(\kappa_{xy}/T)$ on $\mu_0 H/T$. The inset of (b) shows exponential $T$ dependence of the field-independent term $\kappa_{xy}^0$ from
Eq. (2), from which the anisotropy gap $\Delta_A$ was extracted. The red and gray lines in (b) and its inset are guides to the eye.

Figure 4: The initial slope $[\kappa_{xy}/(TB_{ext})]_0$ of the thermal Hall conductivity in the PM and C-FM states of Yb$_2$Ti$_2$O$_7$. (a) $[\kappa_{xy}/(TB_{ext})]_0$ starts to increase below $T$=3 K, the energy scale of the dominant magnetic interaction. Grey symbols represent data recorded in a dilution refrigerator, while black data points were recorded in a He-3 insert. (b) A maximum of $[\kappa_{xy}/(TB_{ext})]_0$ is observed above the critical temperature $T_C$ for long-range magnetic order. (c) The specific heat $c_P(T)$ data from Arpino et al. shows a sharp peak at $T_C$. Dashed red lines in (b,c) at $T_C$ = 0.26 K are guides to the eye. The transition
temperature for the thermal transport sample (a,b) is $T_C = 0.260 \text{ K}$, while the sample for specific heat measurements (c) orders at $T_C = 0.275 \text{ K}$. 