

Thermal Conductivity of the Quantum Spin Liquid Candidate $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$: No Evidence of Mobile Gapless Excitations

P. Bourgeois-Hope,¹ F. Laliberté,¹ E. Lefrançois,¹ G. Grissonnanche,¹ S. René de Cotret,¹ R. Gordon,¹ S. Kitou,² H. Sawa,² H. Cui,³ R. Kato,³ L. Taillefer^{1,4,*} and N. Doiron-Leyraud^{1,†}

¹*Institut Quantique, Département de Physique & RQMP, Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada*

²*Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan*

³*RIKEN, Wako-shi, Saitama 351-0198, Japan*

⁴*Canadian Institute for Advanced Research, Toronto, Ontario M5G 1M1, Canada*



(Received 25 April 2019; revised manuscript received 4 September 2019; published 10 December 2019)

The thermal conductivity κ of the quasi-2D organic spin-liquid candidate $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ (dmit-131) was measured at low temperatures, down to 0.07 K. We observe a vanishingly small residual linear term κ_0/T , in κ/T vs T as $T \rightarrow 0$. This shows that the low-energy excitations responsible for the sizable residual linear term γ in the specific heat C , seen in C/T vs T as $T \rightarrow 0$, are localized. We conclude that there are no mobile gapless excitations in this spin-liquid candidate, in contrast with a prior study of dmit-131 that reported a large κ_0/T value [Yamashita *et al.*, *Science* **328**, 1246 (2010)]. Our study shows that dmit-131 is in fact similar to κ -(BEDT-TTF)₂Cu₂(CN)₃, another quasi-2D organic spin-liquid candidate where a vanishingly small κ_0/T and a sizable γ are seen. We attribute heat conduction in these organic insulators without magnetic order to phonons undergoing strong spin-phonon scattering, as observed in several other spin-liquid materials.

DOI: [10.1103/PhysRevX.9.041051](https://doi.org/10.1103/PhysRevX.9.041051)

Subject Areas: Strongly Correlated Materials

I. INTRODUCTION

Low-dimensional materials with triangular or Kagome lattices are fertile playgrounds for the realization of a quantum spin liquid (QSL). These systems naturally provide a geometrical frustration that suppresses the ordering of antiferromagnetically coupled spins to well below the scale of their coupling J , leaving the spins in a low-temperature ground state that is highly degenerate and strongly fluctuating, key ingredients of a QSL [1,2]. Notable examples of candidate QSL materials are the quasi-2D triangular organic salts κ -(BEDT-TTF)₂Cu₂(CN)₃ (BEDT) [3] and $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ (dmit-131) [4], as well as herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ [5,6], with its ideal Kagome lattice. In these spin-1/2 systems, early evidence for a QSL ground state came from the absence of magnetic order down to the lowest measured temperature. In dmit-131, for instance, an early study reported an exchange interaction $J \simeq 250$ K from susceptibility measurements but no indication of spin

ordering or a spin gap from NMR measurements down to 1.4 K [4]. Instead, below a temperature on the scale of J , an increase in antiferromagnetic correlations was seen, a clear effect of the magnetic frustration. Similar observations were reported for BEDT [3] and herbertsmithite [5,6].

The Holy Grail in the field of quantum spin liquids is to detect mobile gapless excitations, such as “spinons” with fermionic character [1,2]. The search for thermodynamic and transport signatures of such exotic excitations in a QSL has led to a number of specific heat and thermal conductivity studies. The specific heat C of BEDT [7] and dmit-131 [8] does reveal the presence of low-energy excitations (besides phonons), down to very low temperatures. When plotted as C/T vs T , the data yield a sizable residual linear term as $T \rightarrow 0$ (besides the Schottky term), namely, $\gamma \simeq 20$ mJ/K² mol. Such a residual entropy at the lowest temperatures is a defining property of a spin liquid. And indeed, when the same measurement is performed on related organic insulators in which the ground state either has magnetic order, as in κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl [7], or a nonmagnetic singlet ground state with a large charge gap, as in $\text{Et}_2\text{Me}_2\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ (dmit-221) [8], one finds $\gamma \simeq 0$.

The thermal conductivity κ has an advantage over the specific heat: It is only sensitive to mobile excitations. Localized ones, including the low-temperature nuclear Schottky contribution to specific heat, do not contaminate κ .

*louis.taillefer@usherbrooke.ca

†nicolas.doiron-leyraud@usherbrooke.ca

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International license](https://creativecommons.org/licenses/by/4.0/). Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

In BEDT, $\kappa(T)$ displays an activated behavior at low temperature, pointing to gapped mobile excitations [9]. When plotted as κ/T vs T , the data yield a negligible residual linear term as $T \rightarrow 0$, namely, $\kappa_0/T \simeq 0$. By contrast, a prior study of dmit-131 by the Kyoto group found a large residual linear term $\kappa_0/T \simeq 2$ mW/K² cm [10]. In a metal, this would correspond to an excellent conductor with a residual resistivity $\rho_0 \simeq 12$ $\mu\Omega$ cm (using the Wiedemann-Franz law, $\kappa_0/T = L_0/\rho_0$, where $L_0 = 2.44 \times 10^{-8}$ W Ω /K²). This is a truly remarkable result. If confirmed, it would be direct evidence of highly mobile gapless (fermionic) excitations in a candidate quantum spin liquid.

In this article, we report our own thermal conductivity study of dmit-131. We observe a vanishingly small residual linear term, such that $\kappa_0/T < 0.02$ mW/K² cm in our eight samples. This is 100 times smaller than the value reported by the Kyoto group [10]. We conclude that the thermal conductivity of dmit-131 does not reproducibly display the signature of mobile gapless excitations. We attribute heat conduction in dmit-131 entirely to phonons that undergo strong spin-phonon scattering.

II. METHODS

Samples.—The crystal structure of dmit-131 can be viewed as a quasi-2D arrangement of alternating Pd(dmit)₂ and EtMe₃Sb layers. EtMe₃Sb⁺ is a nonmagnetic closed-shell monovalent cation. The Pd(dmit)₂ molecules form dimers each hosting a single spin-1/2 electron, at the vertices of a triangular lattice with slightly anisotropic exchange interactions. We measured the in-plane thermal conductivity of eight single crystals of dmit-131, coming from five different batches (see Table I). These are labeled C1, C2, C3, D1, D2, E1, F1, and G1, where the letters represent a particular growth batch. All the samples were grown at RIKEN by air oxidation of (EtMe₃Sb)₂[Pd(dmit)₂] (60 mg) in acetone (100 ml) containing acetic acid (7–10 ml) at low temperatures in the range of -11 to 5°C . Our sample F1 was prepared under the same conditions, using the same starting material, as the two samples used in the 2010 study by the Kyoto group (labeled A and B) [10]. Our sample G1 comes from the very same growth batch as sample C of Yamashita’s recent paper [11] and as the samples used in specific heat measurements by the Osaka group [8].

Scanning electron microscopy measurements on samples C1, D1, D2, and E1, after the thermal conductivity measurements, revealed no signs of microcracks down to the sub- μm level. In addition, single crystal x-ray diffraction (XRD) measurements on C1, D2, F1, and G1, also after our transport measurements, revealed a high crystalline quality as evidenced by a low R -factor, typically of the order of 2%–4% [12], which is comparable to values found in pristine specimens of dmit-131. By all measures, our samples are of comparable structural and crystalline quality

as those employed in Refs. [10,11]. Details of our XRD measurements can be found in the Supplemental Material [12].

The heat current was made to flow in the 2D plane of dmit-131. In samples C1, D2, and G1, the current is along the a axis, and in sample C2, it is along the b axis. No significant in-plane anisotropy was observed. The orientation within the plane is not known for our other samples, but this is not crucial because of the weak anisotropy. (Note that sample F1 is made of two single crystals with different orientations; see Supplemental Material [12].) The in-plane orientation is not specified in the 2010 study by the Kyoto group [10]. However, samples C and D of Ref. [11] are a -axis samples, as measured by XRD (Ref. [12]).

To connect wires to the samples, three types of contacts are used: evaporated gold pads (with silver paint on top) for samples C1, C2, C3; carbon paste for samples D2, E1; and GE varnish for samples D1, F1, G1. The leads on all samples are 25- μm silver wires. Sample characteristics are given in Table I.

Measurement technique.—The thermal conductivity was measured using a standard four-point steady-state method, whereby a constant heat current \dot{Q} is injected at one end of a sample whose cold end is connected to a copper block at the reference temperature T_0 . The temperature difference $\Delta T = T^+ - T^-$ is measured at two points along the length of the sample, separated by a distance L . The thermal conductivity κ is given by $\kappa = \dot{Q}/(\Delta T \alpha)$, with the geometric factor $\alpha \equiv A/L$, where A is the cross-sectional area of the sample (width $w \times$ thickness t). The error bar on the absolute value of κ comes mostly from the uncertainty in

TABLE I. List of our eight measured samples, giving the sample label (where the letter refers to a given crystal growth batch), the dimensions, the contact method, and the parameters of the power-law fit of the data to $\kappa/T = a + bT^c$ below 0.55 K (units for a and b are mW/K² cm and mW/K^{2+c} cm, respectively). The combined uncertainty on the sample dimensions gives an overall $\pm 20\%$ error on the geometric factor $\alpha = wt/l$. The last two lines provide the corresponding information for samples A and B of Ref. [10], based on their published fits.

Sample	Dimensions (μm)			a	b	c
	$l \times w \times t$	Contacts				
C1	$400 \times 700 \times 33$	Au pads	–0.016	0.42	0.75	
C2	$450 \times 975 \times 41$	Au pads	–0.020	0.33	0.58	
C3	$538 \times 614 \times 35$	Au pads	–0.025	0.23	0.61	
D1	$670 \times 900 \times 60$	GE	–0.019	0.29	0.66	
D2	$550 \times 1000 \times 60$	Carbon	–0.019	0.19	0.69	
E1	$550 \times 1000 \times 60$	Carbon	–0.041	0.24	0.56	
F1	$500 \times 550 \times 20$	GE	–0.012	0.30	0.74	
G1	$540 \times 575 \times 15$	GE	–0.012	0.21	0.70	
A	$1000 \times 1000 \times 50$	Carbon	1.928	57.5	2.0	
B	$1000 \times 1000 \times 50$	Carbon	1.095	31.5	2.0	

measuring the geometric factor, approximately $\pm 20\%$ for all our samples.

The heat current was generated by sending an electric current through a 10-k Ω strain gauge whose resistance is independent of temperature and magnetic field. The temperatures T^+ and T^- were measured using RuOx chips for $T < 4$ K and Cernox sensors for $T > 4$ K, calibrated *in situ* during the measurement. The applied current was chosen such that $\Delta T/T_0 \simeq 4\text{--}10\%$; the resulting κ was independent of ΔT , indicating that there were no heat losses. Measurements below 4 K were performed in a dilution refrigerator, and in a VTI for $T > 4$ K. The samples were always cooled slowly from room temperature, at a rate slower than 10 K per hour. Tests with a faster cooling rate did not produce a significant difference in the data.

III. RESULTS

In Fig. 1, we show the thermal conductivity κ of all our dmit-131 samples, plotted as κ/T vs T , in zero field. We see that all samples display the same qualitative behavior; namely, κ/T decreases smoothly to zero with decreasing T , following a sublinear T dependence. In Fig. 1(a), we compare samples from the same batch (C) but with different current directions: along the a axis for C1 and the b axis for C2. The shape and magnitude of the $\kappa(T)$ curves are very similar, with no pronounced anisotropy. Sample C3 from the same batch yields a qualitatively very similar curve, only smaller by a factor 2 or so. In Fig. 1(b), we compare samples from the same batch (D) but with different types of contact: GE varnish for D1 and carbon paste for D2. There is no qualitative difference. In Fig. 1(c), we directly compare samples C1, F1, and G1, which are from different batches and have different contacts (Au pads for C1, and GE varnish for F1 and G1). In the inset, we see that they have the exact same temperature dependence, *modulo* a multiplicative factor of up to 2.0. As shown in Fig. 2, this temperature dependence is well described below 0.5 K by a power law of the form $\kappa/T = a + bT^c$, where the parameter a is negligibly small, being equal to -0.016 mW/K² cm for C1 and -0.012 mW/K² cm for F1 and G1 (values for all our samples are given in Table I). This shows that κ/T extrapolates to a negligible residual linear term in the $T = 0$ limit, so $\kappa_0/T \simeq 0$. Using instead a linear fit ($c = 1.0$) below 0.2 K also yields a negligibly small a . Leaving aside empirical fits, the lowest data point in sample F1, $\kappa/T = 0.03$ mW/K² cm at $T = 75$ mK (Fig. 2), imposes an upper bound on the residual linear term of this sample of $\kappa_0/T \simeq 0.02$ mW/K² cm.

Finally, to examine the anisotropy of the in-plane thermal conductivity in a single specimen, D1 is measured with a current along one planar direction; then, its contacts are rotated by 90°, and it is remeasured. As seen in Fig. 3, κ is very similar for both orientations, *modulo* a multiplicative factor of 1.27, which is within the combined uncertainty on the geometric factors. Considering all the

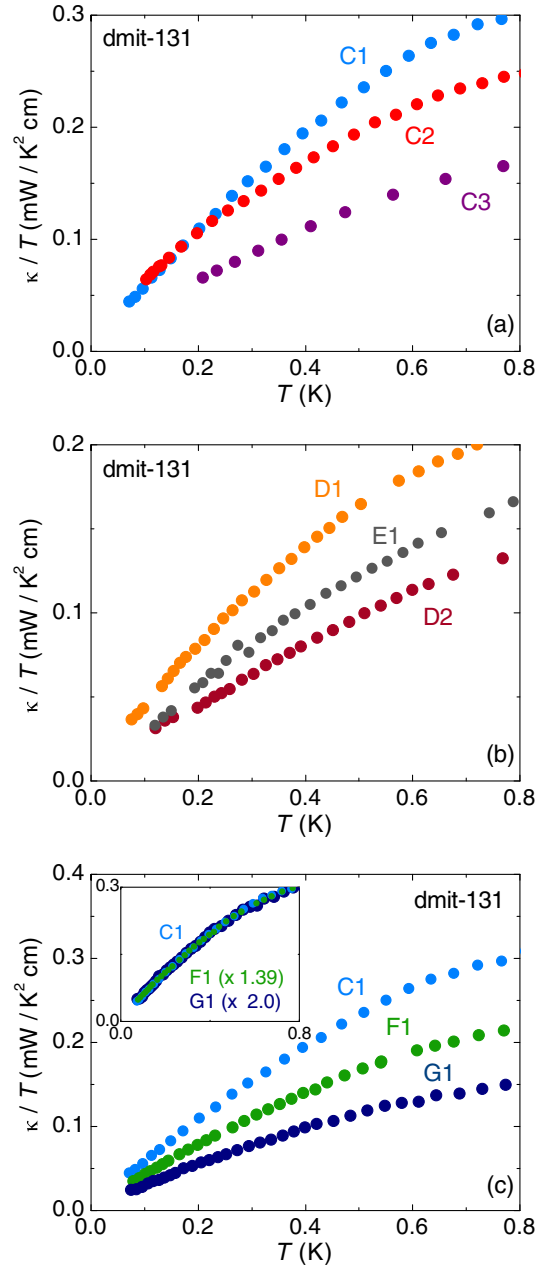


FIG. 1. Thermal conductivity $\kappa(T)$ of dmit-131, expressed as κ/T vs T , for samples C1, C2, C3 (a), samples D1, D2, E1 (b), and samples C1, F1, G1 (c). All data are in zero magnetic field. In panel (c), the inset compares data for C1 with the data for F1 and G1 multiplied by 1.39 and 2.0, respectively.

data, we conclude that there is no qualitative difference—and little quantitative difference—between the five growth batches, the three different types of contacts, and the two current directions, and that $\kappa_0/T \simeq 0$ in dmit-131, with an upper bound of approximately 0.02 mW/K² cm.

Comparison to Kyoto data.—In Fig. 4, we reproduce the Kyoto data of Yamashita and colleagues [10] and compare them with ours. Note the two distinct y-axis scales for their data (left axis) and our data (right axis), which differ by a

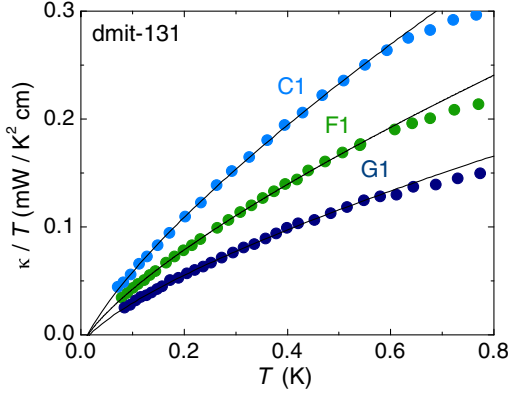


FIG. 2. Same data as in Fig. 1, for samples C1, F1, and G1. The black lines is a fit to $\kappa/T = a + bT^c$ below 0.5 K. The resulting fit parameters (a, b, c) are listed in Table I for all samples.

factor of 10 and 7.5 in Figs. 4(a) and 4(b), respectively. As readily seen, there is a massive quantitative discrepancy between the Kyoto data and the Sherbrooke data. At $T = 0.1$ K, $\kappa/T = 2.5$ mW/K² cm in their sample A [Fig. 4(a)], compared to $\kappa/T = 0.05$ mW/K² cm in our sample F1—a factor 50. At $T = 0.7$ K, $\kappa/T = 13$ mW/K² cm in their sample A [Fig. 4(b)], compared to $\kappa/T = 0.3$ mW/K² cm in our sample C1—a factor 40. There is also a qualitative difference between the two data sets. As seen in Fig. 4(a), the Kyoto data for both of their samples (A and B) show an upward curvature in κ/T vs T , whereas all our samples show a downward (sublinear) curvature. The published power-law fits to their data yield $c \simeq 2$, whereas we get $c < 1$ (Table I). A T^2 fit to the Kyoto data yields a huge residual linear term [Fig. 4(a)]: $\kappa_0/T \simeq 1.9$ mW/K² cm in sample A and $\kappa_0/T \simeq 1.1$ mW/K² cm in sample B. This result is 50–100 times larger than the upper bound on κ_0/T allowed by our data.

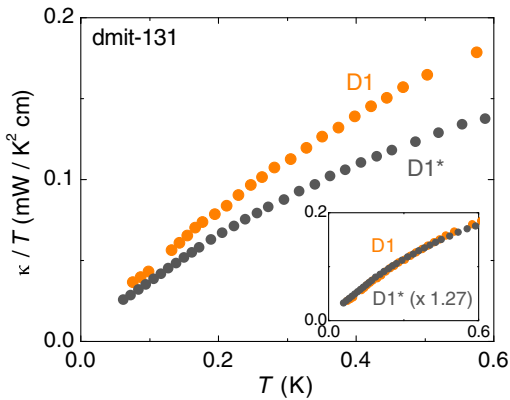


FIG. 3. Same data as in Fig. 1(b) but for sample D1. D1* is the same sample but with contacts rotated in the plane by 90° with respect to D1. Both orientations show the same temperature dependence. As seen in the inset, a multiplicative factor of 1.27 collapses the D1* data onto the D1 data. This shows that there is no large in-plane anisotropy of κ in dmit-131.

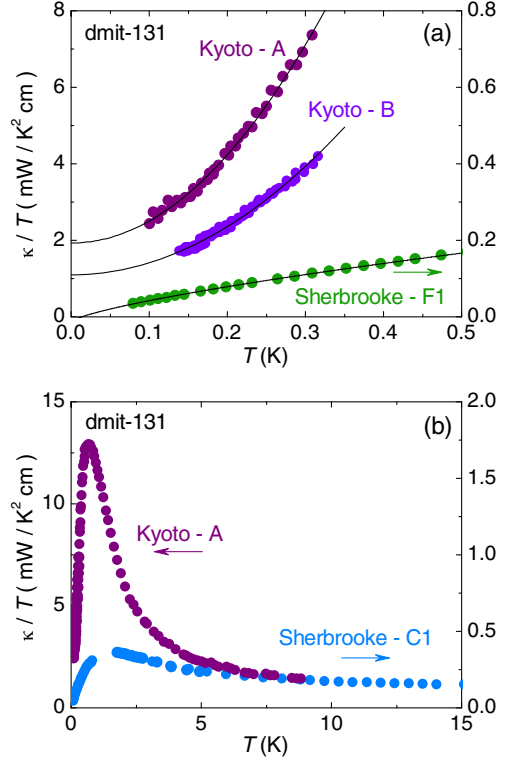


FIG. 4. (a) κ/T vs T for our sample F1 (green, right scale) and for samples A (purple) and B (violet) of Ref. [10] (left scale). Note that the left and right vertical scales differ by a factor 10. The three samples were grown in identical conditions, using the same starting material. For our data, the black line is the free power-law fit below 0.55 K shown in Fig. 2. For the Kyoto data, the lines are quadratic fits reproduced from Ref. [10]. (b) κ/T vs T up to 15 K for our sample C1 (blue, right scale) and for sample A of Ref. [10] (purple, left scale). Note that the left and right vertical scales differ by a factor 7.5.

IV. DISCUSSION

Our data on dmit-131 and those of the Kyoto group are in marked contrast. We note, however, that their thermal conductivity data on BEDT, another organic quasi-2D insulator with a spin-liquid ground state, show κ/T smoothly going to zero with decreasing T [9]. The vanishing of κ/T initially follows a sublinear T dependence, as we observe in dmit-131. So at very low temperature and zero field, there is no significant difference in the thermal conductivity of the two materials, as indeed there is little difference in their specific heat $C(T)$ [7,8].

In the absence of a residual linear term κ_0/T in the thermal conductivity of dmit-131 and BEDT, we conclude that the excitations that give rise to the residual linear term γ in the specific heat of those two materials are not mobile but localized. In this context, it is difficult to know whether spin excitations make any heat-carrying contribution to $\kappa(T)$. The conservative view is to assume that all heat conduction is due to phonons, i.e., $\kappa = \kappa_{\text{ph}}$. Of course, the localized spin excitations at very low temperatures will scatter

phonons, if there is any spin-phonon coupling. As it turns out, this scenario is clearly realized in a number of spin-liquid materials.

The pyrochlore material $\text{Tb}_2\text{Ti}_2\text{O}_7$ does not show any magnetic order down to the lowest temperature [13], as a result of geometrical frustration, reaching instead a highly degenerate spin-ice state in the ground state. Owing to spin-phonon scattering, the thermal conductivity of $\text{Tb}_2\text{Ti}_2\text{O}_7$ is massively suppressed relative to its isostructural nonmagnetic analog $\text{Y}_2\text{Ti}_2\text{O}_7$, a simple insulator without magnetic moments. At $T = 0.3$ K, the phonon mean free path in $\text{Y}_2\text{Ti}_2\text{O}_7$ is set by the sample dimensions, when phonon motion becomes limited by boundary scattering. By contrast, in $\text{Tb}_2\text{Ti}_2\text{O}_7$, the phonon mean free path at $T = 0.3$ K is 200 times smaller [14] because phonons are strongly scattered by spins in the spin-ice state.

Another example of spin-phonon scattering is provided by the hyperkagome antiferromagnet $\text{Na}_{3+x}\text{Ir}_3\text{O}_8$, which can be tuned from a spin-liquid-like insulator to a metal by reducing the Na content [15]. In the insulator, the scattering of phonons off the gapless magnetic excitations (detected in the low-temperature specific heat) causes a reduction in κ_{ph} by a factor 25 at $T = 1$ K relative to the metal [15].

Spin-phonon scattering is also clearly observed in YbMgGaO_4 [16] and RuCl_3 [17]. The spin-liquid candidate YbMgGaO_4 displays strong magnetic excitations visible as a power-law dependence of the specific heat, but its thermal conductivity is dominated by phonons that are scattered by these excitations [16]. RuCl_3 has recently attracted considerable attention as a Kitaev honeycomb magnet. When a field fully suppresses the zigzag magnetic order at about 7.5 T, the phonon-dominated thermal conductivity of RuCl_3 reaches a minimum because of scattering by spin excitations [17].

In Fig. 5, we compare the thermal conductivity of these four materials with that of dmit-131 as reported by the Kyoto group [10], the Fudan group [18], and us. We see that our data and those of the Fudan group agree well with those typical of spin-liquid materials but that the Kyoto data are anomalously large, by a factor of 20 or more. This result reveals a fundamental problem with the Kyoto data: Their phonon conductivity κ_{ph} is enormous (see samples A, B, C, and D of Ref. [11]). It corresponds roughly to the value expected if the phonon mean free path is the size of the sample (Fig. 2 in Ref [11]), which means that nothing scatters phonons at low temperature, which is physically unrealistic. The fundamental property of a gapless spin liquid is the presence of zero-energy spin excitations, which show up in a finite residual term γ in the specific heat. Those spin excitations will scatter phonons down to very low T , much like electrons in a metal scatter phonons down to very low T . We know of no gapless spin-liquid candidate whose κ_{ph} is not strongly reduced from its maximal boundary-limited value.

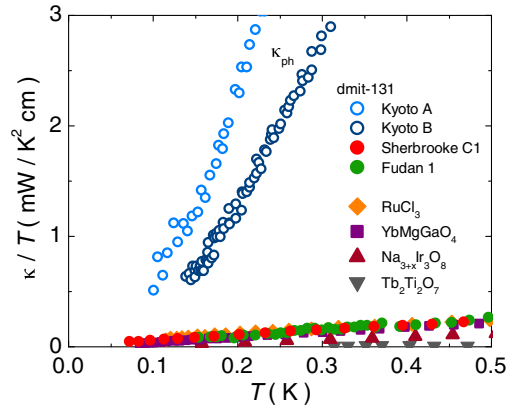


FIG. 5. Thermal conductivity κ/T vs T for dmit-131, as reported by the Kyoto group [10], the Fudan group [18], and in the present work. For the Kyoto data, the residual linear term has been subtracted so that the data reflect only the phonon contribution κ_{ph} . For comparison, thermal conductivity data for the spin-liquid materials RuCl_3 [17], YbMgGaO_4 [16], $\text{Na}_{3+x}\text{Ir}_3\text{O}_8$ [15], and $\text{Tb}_2\text{Ti}_2\text{O}_7$ [14] are also plotted. These are all insulators, so the thermal conductivity is entirely phononic and is at least 20 times smaller than κ_{ph} in the Kyoto data.

We therefore propose that phonons in dmit-131 (and BEDT) are also scattered by the low-energy spin excitations of their spin-liquid state at low temperatures. In Fig. 6, we compare our data on sample F1 to the calculated value of κ_{ph} assuming the phonon mean free path ℓ_{ph} is limited only by the sample boundaries, so that $\ell_{\text{ph}} = 2\sqrt{wt}/\pi = 120 \mu\text{m}$ (Table I), using the standard formula, $\kappa_{\text{ph}} = C_{\text{ph}}v_{\text{ph}}\ell_{\text{ph}}/3$ [19], where $C_{\text{ph}} = \beta T^3$ is the phonon specific heat of dmit-131, with $\beta = 24 \text{ mJ/K}^4 \text{ mol}$ ($47 \text{ J/K}^4 \text{ m}^3$ given 4 units of chemical formula per unit cell) [8], and v_{ph} is the phonon velocity, taken to be 2000 m/s. We find $\kappa_{\text{ph}} = 37 T^3 \text{ mW/K cm}$ in the boundary scattering limit, which, at $T = 0.3$ K, is roughly 30 times larger than the measured value.

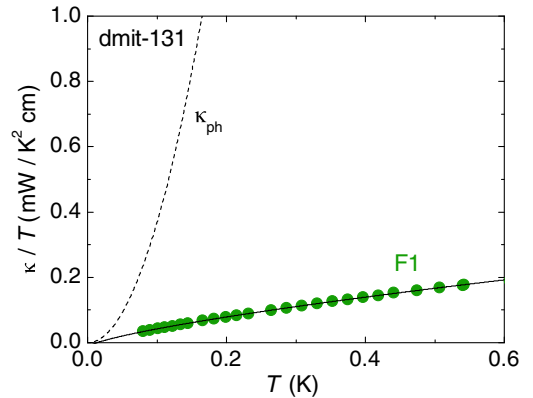


FIG. 6. The same data (green dots) and fit (full line) as in Fig. 2, for sample F1. For comparison, the dashed line is the phonon thermal conductivity expected for that sample if phonons were only scattered by the sample boundaries (see text).

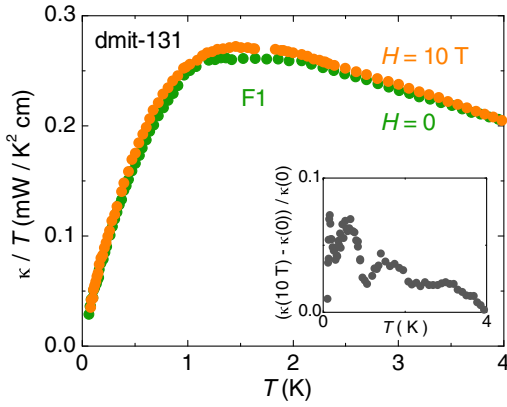


FIG. 7. Thermal conductivity of our sample F1, plotted as κ/T vs T , in both zero field (green) and at $H = 10$ T (orange), revealing a weak field dependence up to 4 K. Inset: Relative change in $\kappa(T)$ due to a magnetic field $H = 10$ T, plotted as $[\kappa(10\text{T}) - \kappa(0)]/\kappa(0)$ vs T .

In a scenario where phonons are scattered by spin excitations, one might expect the spin spectrum to be dependent on magnetic field and thus κ_{ph} to be field dependent. In Fig. 7, we see that applying 10 T normal to the 2D planes does increase κ in dmit-131 but only very slightly, by no more than 5% below 4 K. The weakness of the effect is consistent with the effect of field on the specific heat of dmit-131, which is no more than 5% below 4 K [8]. Not shown here, our data for a field of 10 T applied in the plane are essentially identical to those shown in Fig. 7.

A possible explanation for the unusual low-temperature behavior of both $C(T)$ and $\kappa(T)$ in dmit-131 (and BEDT) is provided by a recent theory of local singlets in a quantum paramagnet with frustration, which appear as defects in a triangular lattice of spin-1/2 moments [20]. These local singlets give rise to a specific heat that grows as $C \propto T^{0.7}$ from $T = 0$, and they scatter phonons in such a way that $\kappa_{\text{ph}} \propto T^2$. Another scenario is based on an $S = 1/2$ Heisenberg antiferromagnet on a triangular lattice with quenched randomness in the exchange interaction [21], whose quantum spin-liquid ground state has gapless excitations that give $C \propto T$.

Finally, we note that nuclear magnetic resonance measurements on dmit-131 [4,22] reveal a vanishing dynamical susceptibility at low temperatures, which excludes fully gapless fermionic magnetic excitations in its ground state. This case is entirely consistent with our finding that no gapless fermionic excitations contribute to the heat transport, but it is hard to reconcile with the conclusion of Yamashita and colleagues, which shows that the physics of dmit-131 must be seriously reexamined.

Soon after our paper was first posted, Yamashita published a note [11] to propose a possible explanation for the huge discrepancy between our data and the data they reported in 2010 [10]. Importantly, whereas in 2010 only data from two samples (A and B) were reported, in this note

Kyoto data from an additional four dmit samples are presented (samples C, D, E, and F). We learn that κ in their samples E and F is 50–100 times smaller than κ in samples A and B. This dramatic lack of reproducibility in measurements performed on nominally identical samples from a single source is cause for concern.

Yamashita suggests that strong sample dependence could come from either structural domains that originate from the disordered cations, microcracks, or different impurity levels. Impurities cannot be the cause of the huge difference between our sample F1 and the Kyoto samples A and B since the same starting materials were used to grow these samples. Our sample G1 and Yamashita’s sample C (Ref. [11]) both come from the same growth batch. As mentioned in Sec. II and detailed in the Supplemental Information (Ref. [12]), we performed careful XRD analysis, which revealed high crystal quality for all samples. This system has the degree of freedom of coordination of the ethyl group in the cation EtMe_3Sb^+ . In the refinement of the structural model, however, the orientation is averaged due to space group constraints. Using high-intensity synchrotron radiation, orientational ordering at cryogenic temperatures can be clarified by analyzing the domain formation. However, the ethyl group ordering and domain formation associated therewith in this system could not be determined precisely due to strong effects of the thermal vibration even at 100 K. It should be noted that there was no significant difference in the pattern of thermal diffuse scattering at 100 K between our crystals and the Kyoto samples. Finally, scanning electron microscopy characterization of our samples does not reveal the presence of any microcracks.

Yamashita mentions that the high value of the phonon conductivity κ_{ph} measured in their “high- κ ” samples (A, B, C, D) is comparable to the value of κ_{ph} measured in other organic materials. However, the comparison is not so simple because the two materials he mentions that were measured by other groups, namely $\kappa\text{-ET}_2\text{Cu}(\text{NCS})_2$ [23] and $\lambda\text{-(BETS)}_2\text{GaCl}_4$ [24], are not insulators but metals (and superconductors at low temperatures).

In the superconducting state, electron states are gapped, so two things happen: The electronic contribution κ_{el} is reduced, and κ_{ph} is increased because phonons are less scattered by electrons. Applying a magnetic field to suppress superconductivity clearly shows that κ_{el} increases and κ_{ph} decreases. In Fig. 8(a), we compare Kyoto’s dmit-131 data (samples A and B) with data on $\kappa\text{-ET}_2\text{Cu}_2(\text{NCS})_2$ in the superconducting state, at $H = 0$ (for the two samples reported in Ref. [23]). We see that the thermal conductivity of $\kappa\text{-ET}_2\text{Cu}_2(\text{NCS})_2$ lies roughly halfway between the Kyoto data and our data on dmit-131. This result shows that even when superconductivity gaps out the low-energy excitations in $\kappa\text{-ET}_2\text{Cu}_2(\text{NCS})_2$, the phonons in that material do not conduct nearly as well as they appear to in Kyoto’s samples of dmit-131, a material whose low-energy excitations are not gapped (as seen in specific heat).

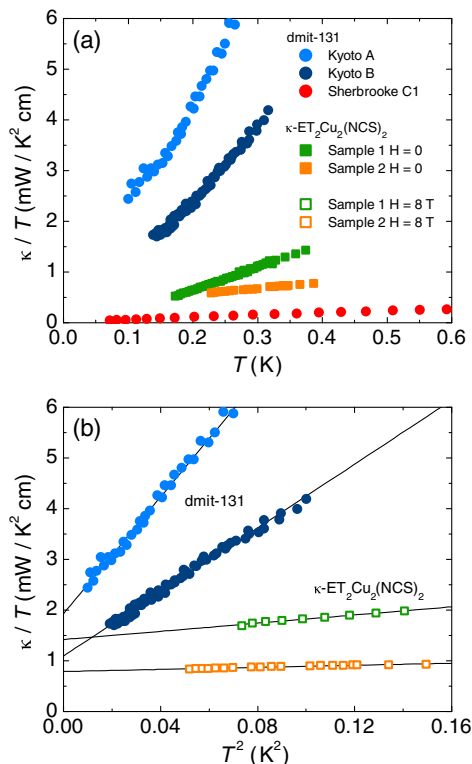


FIG. 8. (a) Thermal conductivity κ/T vs T for dmit-131 (dots) as measured by the Kyoto group and at Sherbrooke, and for $\kappa\text{-ET}_2\text{Cu}_2(\text{NCS})_2$ (squares) as reported in Ref. [23]. All data are in $H = 0$, meaning that $\kappa\text{-ET}_2\text{Cu}_2(\text{NCS})_2$ is in the superconducting state (full squares) where low-energy excitations are gapped and cannot scatter phonons. (b) Thermal conductivity κ/T vs T^2 for Kyoto dmit-131 data and $\kappa\text{-ET}_2\text{Cu}_2(\text{NCS})_2$ in its nonsuperconducting state in $H = 8$ T (open squares), which reveals a comparable residual linear term but a much smaller phonon slope in $\kappa\text{-ET}_2\text{Cu}_2(\text{NCS})_2$. The lines are a fit of the data to $\kappa/T = a + bT^2$.

In Fig. 8(b), we compare Kyoto’s dmit-131 data with data for $\kappa\text{-ET}_2\text{Cu}_2(\text{NCS})_2$ now measured in the normal state, at $H = 8$ T (Ref. [23]). We see that the residual linear term in the thermal conductivity of $\kappa\text{-ET}_2\text{Cu}_2(\text{NCS})_2$ is comparable to that reported for Kyoto’s high- κ dmit-131 samples (A, B, C, D). However, the phonon slope is now much smaller, by a factor ranging between 10 and 50. The low value of κ_{ph} in the normal state of $\kappa\text{-ET}_2\text{Cu}_2(\text{NCS})_2$ is natural—this is what is observed in any metal. It appears unphysical to have phonons propagating in a sea of zero-energy spin excitations and, at the same time, display a conductivity as if these excitations were absent, as Kyoto’s dmit-131 data on samples A, B, C, and D suggest.

This idea raises a fundamental question about the Kyoto data on samples with a large residual linear term (A, B, C, D)—comparable, in fact, to that measured in the metal $\kappa\text{-ET}_2\text{Cu}(\text{NCS})_2$ (see lower panel of Fig. 8). How is it possible that phonons in dmit-131 are not scattered by the zero-energy spin excitations that give rise to the residual

linear term in the specific heat? In a metal with electrons, κ_{ph} is strongly reduced because phonons are scattered by electrons—as observed in $\kappa\text{-ET}_2\text{Cu}(\text{NCS})_2$ (Fig. 8). In other spin-liquid materials, κ_{ph} is also strongly reduced (Fig. 5). We see no reason why phonons in dmit-131 should be entirely decoupled from the low-energy spin excitations.

V. SUMMARY

We measured the thermal conductivity of eight single crystals of dmit-131 at temperatures down to 70 mK, using three different types of contacts, and we found that all data are consistent with a power-law dependence below $T \simeq 0.5$ K, namely, $\kappa/T = a + bT^c$, with a negligible residual linear term ($a \simeq 0$), a sublinear power ($c \simeq 0.7$), and a magnitude that varies by a factor 2 or so. The strong similarity of $\kappa(T)$ reported here for dmit-131 and BEDT [9] is consistent with their very similar specific heat $C(T)$. We attribute the magnitude and behavior of $\kappa(T)$ entirely to phonons as the sole carriers of heat, which are scattered by low-energy spin excitations of the spin-liquid state, which is typical of spin-liquid materials.

Our data on dmit-131 are in sharp disagreement with those of Ref. [10], where $\kappa(T)$ for dmit-131 is 50 times larger, with a quadratic T dependence of κ/T ($c = 2.0$), extrapolating to a large residual linear term as $T \rightarrow 0$ ($a \equiv \kappa_0/T \simeq 2$ mW/K² cm). Our samples come from the same source as those used by Yamashita and colleagues: in one case (F1) grown using the very same starting material and in another case (G1) coming from the same growth batch as sample C of Ref. [11]. Moreover, scanning electron microscopy measurements have shown that no microcracks are present in our samples, and XRD measurements have demonstrated that our samples—both before and after our thermal conductivity measurements—are of similar quality as those employed by Yamashita and coworkers. Consequently, it is unlikely that the sample quality could explain the disagreement between our study and prior work [10,11]. Thus, we are left with no compelling, robust, reproducible experimental evidence of mobile gapless excitations in the low-temperature thermal conductivity of any candidate spin liquid.

ACKNOWLEDGMENTS

We thank L. Balents, K. Behnia, B. Fauqué, H. Kawamura, P. Lee, S. Li, J. Quilliam, T. Senthil, and W. Witczak-Krempa for stimulating discussions. We thank S. Fortier for his assistance with the experiments. L. T. acknowledges support from the Canadian Institute for Advanced Research (CIFAR) as a CIFAR Fellow, and funding from the Institut Quantique, the Natural Sciences and Engineering Research Council of Canada (PIN:123817), the Fonds de Recherche du Québec—Nature et Technologies (FRQNT), the Canada Foundation for Innovation (CFI), and a Canada Research Chair. This research was undertaken thanks in part

to funding from the Canada First Research Excellence Fund. This work was partially supported by the JSPS Grant-in-Aids for Scientific Research (S) (Grant No. JP16H06346).

Note added.—Recently, the group of Shiyun Li at Fudan University has obtained results similar to ours from their own thermal conductivity study of dmit-131 [18].

-
- [1] P. A. Lee, *An End to the Drought of Quantum Spin Liquids*, *Science* **321**, 1306 (2008).
- [2] L. Balents, *Spin Liquids in Frustrated Magnets*, *Nature (London)* **464**, 199 (2010).
- [3] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, *Spin Liquid State in an Organic Mott Insulator with a Triangular Lattice*, *Phys. Rev. Lett.* **91**, 107001 (2003).
- [4] T. Itou, A. Oyamada, S. Maegawa, M. Tamura, and R. Kato, *¹³C NMR Study of the Spin-Liquid State in the Triangular Quantum Antiferromagnet EtMe₃Sb[Pd(dmit)₂]₂*, *J. Phys. Conf. Ser.* **145**, 012039 (2009).
- [5] J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Bartlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-H. Chung, D. G. Nocera, and Y. S. Lee, *Spin Dynamics of the Spin-1/2 Kagome Lattice Antiferromagnet ZnCu₃(OH)₆Cl₂*, *Phys. Rev. Lett.* **98**, 107204 (2007).
- [6] P. Mendels, F. Bert, M. A. de Vries, A. Olariu, A. Harrison, F. Duc, J. C. Trombe, J. S. Lord, A. Amato, and C. Baines, *Quantum Magnetism in the Paratacamite Family: Towards an Ideal Kagome Lattice*, *Phys. Rev. Lett.* **98**, 077204 (2007).
- [7] S. Yamashita, Y. Nakazawa, M. Oguni, Y. Oshima, H. Nojiri, Y. Shimizu, K. Miyagawa, and K. Kanoda, *Thermodynamic Properties of a Spin-1/2 Spin-Liquid State in a κ -Type Organic Salt*, *Nat. Phys.* **4**, 459 (2008).
- [8] S. Yamashita, T. Yamamoto, Y. Nakazawa, M. Tamura, and R. Kato, *Gapless Spin Liquid of an Organic Triangular Compound Evidenced by Thermodynamic Measurements*, *Nat. Commun.* **2**, 275 (2011).
- [9] M. Yamashita, N. Nakata, Y. Kasahara, T. Sasaki, N. Yoneyama, N. Kobayashi, S. Fujimoto, T. Shibauchi, and Y. Matsuda, *Thermal-Transport Measurements in a Quantum Spin-Liquid State of the Frustrated Triangular Magnet κ -(BEDT-TTF)₂Cu₂(CN)₃*, *Nat. Phys.* **5**, 44 (2009).
- [10] M. Yamashita, N. Nakata, Y. Senshu, M. Nagata, H. M. Yamamoto, R. Kato, T. Shibauchi, and Y. Matsuda, *Highly Mobile Gapless Excitations in a Two-Dimensional Candidate Quantum Spin Liquid*, *Science* **328**, 1246 (2010).
- [11] M. Yamashita, *Boundary-Limited and Glassy-like Phonon Thermal Conduction in EtMe₃Sb[Pd(dmit)₂]₂*, *J. Phys. Soc. Jpn.* **88**, 083702 (2019).
- [12] P. Bourgeois-Hope, Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevX.9.041051> for details of our x-ray diffraction data and CIF files (2019).
- [13] J. S. Gardner, S. R. Dunsiger, B. D. Gaulin, M. J. P. Gingras, J. E. Greedan, R. F. Kiefl, M. D. Lumsden, W. A. MacFarlane, N. P. Raju, J. E. Sonier, I. Swainson, and Z. Tun, *Cooperative Paramagnetism in the Geometrically Frustrated Pyrochlore Antiferromagnet Tb₂Ti₂O₇*, *Phys. Rev. Lett.* **82**, 1012 (1999).
- [14] Q. J. Li, Z. Y. Zhao, C. Fan, F. B. Zhang, H. D. Zhou, X. Zhao, and X. F. Sun, *Phonon-Glass-like Behavior of Magnetic Origin in Single-Crystal Tb₂Ti₂O₇*, *Phys. Rev. B* **87**, 214408 (2013).
- [15] B. Fauqué, X. Xu, A. F. Bangura, E. C. Hunter, A. Yamamoto, K. Behnia, A. Carrington, H. Takagi, N. E. Hussey, and R. S. Perry, *Thermal Conductivity across the Metal-Insulator Transition in the Single-Crystalline Kagome Antiferromagnet Na_{3+x}Ir₃O₈*, *Phys. Rev. B* **91**, 075129 (2015).
- [16] Y. Xu, J. Zhang, Y. S. Li, Y. J. Yu, X. C. Hong, Q. M. Zhang, and S. Y. Li, *Absence of Magnetic Thermal Conductivity in the Quantum Spin-Liquid Candidate YbMgGaO₄*, *Phys. Rev. Lett.* **117**, 267202 (2016).
- [17] Y. J. Yu, Y. Xu, K. J. Ran, J. M. Ni, Y. Y. Huang, J. H. Wang, J. S. Wen, and S. Y. Li, *Ultralow-Temperature Thermal Conductivity of the Kitaev Honeycomb Magnet α -RuCl₃ across the Field-Induced Phase Transition*, *Phys. Rev. Lett.* **120**, 067202 (2018).
- [18] J. M. Ni, B. L. Pan, Y. Y. Huang, J. Y. Zeng, Y. J. Yu, E. J. Cheng, L. S. Wang, R. Kato, and S. Y. Li, *Absence of Magnetic Thermal Conductivity in the Quantum Spin Liquid Candidate EtMe₃Sb[Pd(dmit)₂]₂—Revisited*, *Phys. Rev. Lett.* **123**, 247204 (2019).
- [19] S. Y. Li, L. Taillefer, C. H. Wang, and X. H. Chen, *Ballistic Magnon Transport and Phonon Scattering in the Antiferromagnet Nd₂CuO₄*, *Phys. Rev. Lett.* **95**, 156603 (2005).
- [20] I. Kimchi, A. Nahum, and T. Senthil, *Valence Bonds in Random Quantum Magnets: Theory and Application to YbMgGaO₄*, *Phys. Rev. X* **8**, 031028 (2018).
- [21] K. Watanabe, H. Kawamura, H. Nakano, and T. Sakai, *Quantum Spin-Liquid Behavior in the Spin-1/2 Random Heisenberg Antiferromagnet on the Triangular Lattice*, *J. Phys. Soc. Jpn.* **83**, 034714 (2014).
- [22] T. Itou, K. Yamashita, M. Nishiyama, A. Oyamada, S. Maegawa, K. Kubo, and R. Kato, *Nuclear Magnetic Resonance of the Inequivalent Carbon Atoms in the Organic Spin-Liquid Material EtMe₃Sb[Pd(dmit)₂]₂*, *Phys. Rev. B* **84**, 094405 (2011).
- [23] S. Belin, K. Behnia, and A. Deluzet, *Heat Conduction in κ -(BEDT-TTF)₂Cu(NCS)₂*, *Phys. Rev. Lett.* **81**, 4728 (1998).
- [24] M. A. Tanatar, T. Ishiguro, H. Tanaka, and H. Kobayashi, *Magnetic Field–Temperature Phase Diagram of the Quasi-Two-Dimensional Organic Superconductor λ -(BETS)₂GaCl₄ Studied via Thermal Conductivity*, *Phys. Rev. B* **66**, 134503 (2002).