Thermodynamic Perspective on Field-Induced Behavior of α-RuCl$_3$

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Measurements of the magnetic Grüneisen parameter (Γ_B) and specific heat on the Kitaev material candidate α-RuCl$_3$ are used to access in-plane field and temperature dependence of the entropy up to 12 T and down to 1 K. No signatures corresponding to phase transitions are detected beyond the boundary of the magnetically ordered region, but only a shoulderlike anomaly in Γ_B, involving an entropy increment as small as $10^{-5}R\log 2$. These observations put into question the presence of a phase transition between the purported quantum spin liquid and the field-polarized state of α-RuCl$_3$. We show theoretically that at low temperatures Γ_B is sensitive to crossings in the lowest excitations within gapped phases, and identify the measured shoulderlike anomaly as being of such origin. Exact diagonalization calculations demonstrate that the shoulderlike anomaly can be reproduced in extended Kitaev models that gain proximity to an additional phase at finite field without entering it. We discuss manifestations of this proximity in other measurements.

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Quantum spin liquids (QSLs) describe novel states of matter that violate Landau's concept of broken symmetry and associated order parameters [1]. These states feature unconventional quasiparticle excitations, such as spinons, Majorana fermions, or artificial photons [2]. For example, the exactly solvable Kitaev model leads to a Z_2 QSL ground state with emergent fractionalized Majorana excitations [3]. Recent efforts focused on compounds with heavy transition-metal elements as experimental realizations of this model [4–7], and several promising materials including the two-dimensional α-RuCl$_3$, Na$_2$IrO$_3$, and α-Li$_2$IrO$_3$ have been identified. Although interactions beyond the Kitaev model cause long-range magnetic order in the above mentioned materials, the presence of a strong Kitaev exchange has been suggested to lead to proximate QSL behavior in the paramagnetic state above the Néel temperature [8–10] and in applied magnetic fields upon the suppression of the ordered phase [11,12].

Here, we focus on α-RuCl$_3$, which magnetically orders below 7 K in zero field [13,14] and reveals magnon excitations at low energies [15–21]. Additionally, it shows broad high-energy spectral features that are often interpreted as fractionalized excitations—vestiges of the proximate QSL state [15,22–25]—although this behavior can also be described in terms of magnon decays and incoherent excitations originating from strong magnetic anharmonicities [26–29]. In-plane magnetic fields lead to a gradual suppression of magnetic order that completely disappears around $B_c^{\mathrm{AF2}} \simeq 7.5$ T [30–34] (see also the inset of Fig. 1 for the data from our study).

The nature of the phase lying immediately above B_c^{AF2} has been a matter of significant debate. On the one hand, it can be seen as a precursor of the gapped fully polarized state [35], but reveals only a fraction of the total magnetization of spin-$\frac{1}{2}$ because of the sizable off-diagonal exchange present in the system [27,36]. On the other hand, if magnetic order is seen as an obstacle to the Kitaev QSL, then the suppression of the ordered phase should give way to the QSL itself. This latter scenario was reinforced by the observation of the quantized half-integer thermal Hall effect, a signature of underlying topological order [37]. This quantization was initially reported at 7–9 T [38], right above B_c^{AF2}, although more recent studies detected quantized behavior only in higher in-plane fields of 8.5–9 T [39] or even 10–12 T [40], suggesting that the putative spin-liquid phase may not emerge from the magnetically ordered phase directly. Importantly, if a topological QSL occurs at intermediate fields, the borders of the phase would have to be marked by distinct thermodynamic signatures [41].

In this Letter, we therefore examine the temperature-field phase diagram of α-RuCl$_3$ by high-resolution thermodynamic measurements and seek to explore phase transitions related to the half-integer plateau in thermal

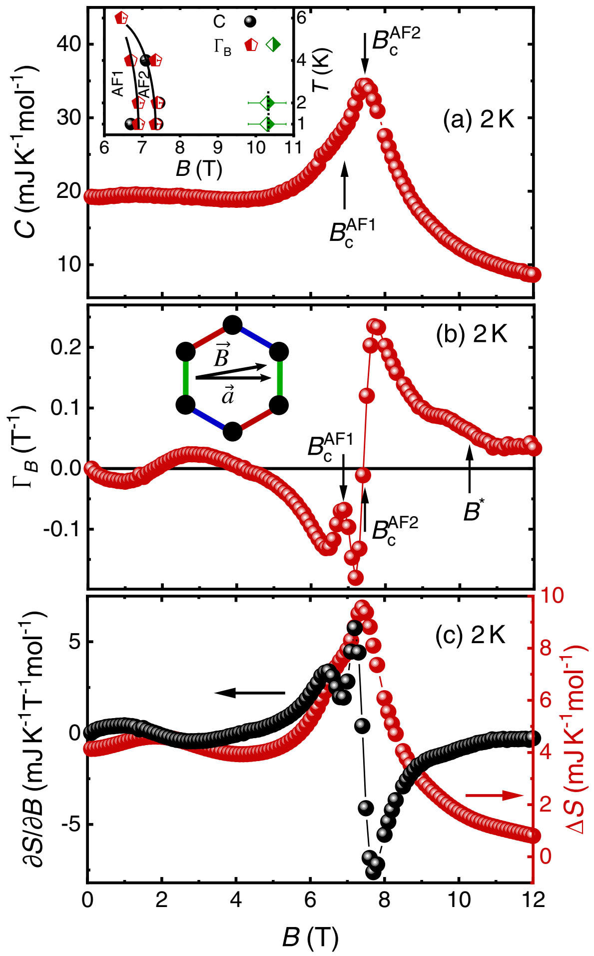

FIG. 1. Magnetic field dependencies of (a) the specific heat C, (b) the magnetic Grüneisen parameter Γ_B, (c) the field derivative of the entropy $\partial S/\partial B$ and entropy increment ΔS (see text) for α-$RuCl_3$ at 2 K. The inset in (a) shows a temperature-field phase diagram derived from our data, where solid lines stand for thermodynamic transitions and the dotted line for a crossover at B^*, and in (b) the field direction of our experiment.

Hall effect of Refs. [38–40]. We find that no phase transitions occur for fields above B_c^{AF2}, whereas the previously reported shoulder anomalies in the magnetocaloric coefficient [18] and magnetostriction [42] above 8 T are likely due to a change in the nature of the lowest excited states with only a tiny change in entropy. This casts doubts on the existence of an intrinsic phase transition between the purported QSL and the partially polarized phase of α-$RuCl_3$. We analyze the possible microscopic origin of the observed shoulder anomaly via finite-temperature exact diagonalization for realistic spin models for α-$RuCl_3$ [26,43,44]. Our results suggest that this feature may originate from crossings of low-lying excitations related to competing distinct phases, without the system experiencing a phase transition to a new phase.

Measurements of the magnetic Grüneisen parameter (Γ_B) and specific heat (C) as a function of field were performed with a dilution refrigerator using the high-resolution alternating-field method for Γ_B [45] and the quasiadiabatic heat pulse and relaxation method for C [46]. High-quality single crystals were grown by vacuum sublimation [55]. Sample quality was checked by a zero-field heat-capacity measurement. The sample showed a single phase transition around 7 K and no signatures of an additional phase transition at 14 K, which could be caused by stacking faults. The zero-field measurement repeated after the measurements in the magnetic field confirmed that the sample remained intact, with no stacking faults introduced during the experiment [46].

From previous works on α-$RuCl_3$ it is known that the magnetic phase diagram varies somewhat for different in-plane field directions [56]. For fields applied perpendicular to the Ru-Ru bonds (crystallographic a direction), one observes an extended region of an intermediate ordered phase [56], which is stable between B_c^{AF1} and B_c^{AF2}, and presumably related to a change of the out-of-plane ordering wave vector [57]. The half-integer thermal Hall effect was observed for $B\|a$ [38–40], whereas from symmetry considerations no thermal Hall effect is expected for $B\|b$ [40,58]. For our measurements, we choose a field direction 10° away from $\vec{a}$ [Fig. 1(b)] following the setting of Ref. [18].

In Fig. 1, we show both specific heat C and the magnetic Grüneisen parameter $\Gamma_B = -(\partial M/\partial T)/C = (1/T)(\partial T/\partial B)_S$, which quantifies the ratio between the temperature derivative of the magnetization and the specific heat. Γ_B is a measure of the adiabatic magnetocaloric effect and a very sensitive probe of classical and quantum phase transitions [59–61]. Using the high-resolution alternating-field method [45], we determine the magnetocaloric effect under perfect adiabatic conditions, in contrast to the previous magnetocaloric study of Ref. [18]. Combining Γ_B with the specific heat provides access to the temperature derivative of the magnetic entropy across the phase diagram as $\partial S/\partial B = -C\Gamma_B$.

In the specific heat, shown in Fig. 1(a), the dominant feature is a peak at $B_c^{AF2} = 7.4$ T. At the same field, Γ_B exhibits a sharp jump with a sign change from negative to positive, cf. Fig. 1(b). We note that entropy S generally exhibits a maximum at a second-order phase transition between the magnetically ordered and paramagnetic phases [60]. The entropy change across the transition, $\Delta S = -\int dBC\Gamma_B$ [Fig. 1(c)], indeed shows a maximum, because C is always positive, and a sign change of Γ_B from negative to positive with increasing field corresponds to a maximum in the entropy at B_c^{AF2}.

Another anomaly at $B_c^{AF1} = 6.9$ T is also clearly visible as a local maximum of Γ_B, although a corresponding feature in C is nearly absent. For a weak first-order phase transition one also expects a maximum of the entropy, but without a discontinuity in C if the transition is significantly smeared out. In this case, $\partial S/\partial B$ goes

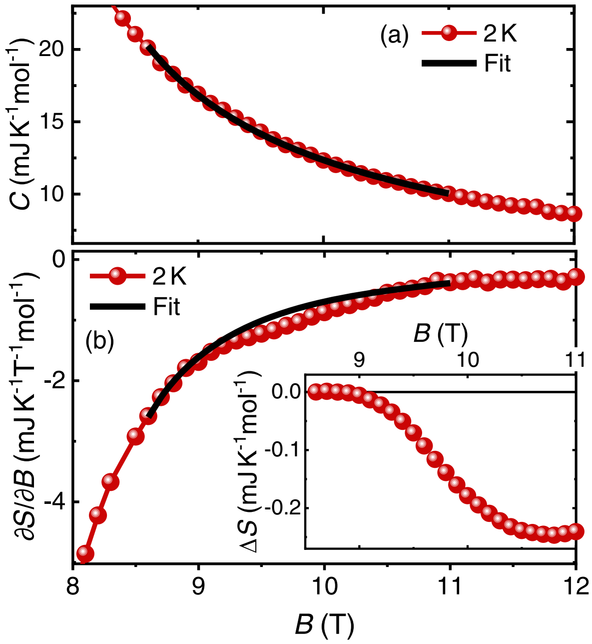

FIG. 2. Magnetic field dependence of the specific heat (a) and field derivative of the entropy (b), as well as the entropy change (inset) for α-$RuCl_3$ at 2 K between 8 and 12 T. The black solid lines indicate $C = \beta(B - B_c)^\epsilon$ with $B_c^{AF2} = 7.4$ T, $\beta = 22.7(9)$ mJK^{-1} mol^{-1} T$^{-\epsilon}$, and $\epsilon = 0.64(5)$ (a), and $\partial S/\partial B = \beta(B - B_c)^\epsilon G_r/(B - B_c)$ (b), with $G_r = -0.157(2)$, respectively [46]. The inset shows the difference between the measured entropy and the integration of the above function for $\partial S/\partial B$ for fields between 8.6 and 11 T.

through a minimum that causes a maximum in Γ_B without the jump and sign change. This way, we interpret B_c^{AF1} as a first-order phase transition, which is compatible with the reported change in the magnetic propagation vector at this field [57]. We note in passing that there is another sign change in Γ_B at 1.8 T, indicating an additional entropy maximum. It is mostly likely related to the domain reconstruction reported in previous studies [31].

Beyond B_c^{AF2}, the antiferromagnetic (AF) order is destroyed. At higher fields, if a QSL phase exists, at least one additional phase transition is necessary when the QSL is suppressed, as indicated by the disappearance of the half quantization in the thermal Hall effect [38]. However, we find no signature of a further phase transition in our specific heat data [Fig. 2(a)]. We find only a broad shoulder in Γ_B centered at $B^* \sim 10$ T, which is much weaker than the two other anomalies. From these observations, we conclude that there is no second-order phase transition above B_c^{AF2} within the resolution of our experiment. As shown in the phase diagram (Fig. 1), the shoulder at B^* is observed also at 1 K, but not above 2 K [46]. According to recent Raman [19,20] and neutron-scattering [18] experiments, the field range of the shoulder falls into the region of a gapped phase.

To obtain further information on the shoulderlike anomaly at B^* in the magnetic Grüneisen parameter, we inspect the entropy contained in different transition anomalies using $\partial S/\partial B = -C\Gamma_B$ shown in Fig. 1(c). Two clear jumps are observed at B_c^{AF1} and B_c^{AF2}, whereas at B^* only a broad shoulder can be distinguished [Fig. 2(b)]. Clearly, the anomaly near B^* results in a negative contribution to $\partial S/\partial B$ and thus also to an additional decrease in the magnetic entropy. Qualitatively, this may indicate that the state for $B > B^*$ has lower entropy, which naturally arises due to the polarization of moments by magnetic field.

By subtracting the background [46] and integrating $\partial S/\partial B$, we estimate that only a tiny amount of entropy, 0.25 mJ/mol $\cdot$ K $(4.3 \times 10^{-5} R \log 2)$, is associated with the shoulder at B^*. For comparison, the entropy change at B_c^{AF2} is 12.5 mJ/mol $\cdot$ K and thus 50 times larger. Although entropy changes generally become small at low temperatures, they are not expected to become so tiny, especially at the transition between a chiral Kitaev spin liquid and polarized state, where the flux gap is closed and low-energy excitations are abundant [62,63].

To analyze our experimental results in the context of realistic Hamiltonians of α-$RuCl_3$, we first perform exact diagonalization calculations on the two-dimensional *ab initio* guided minimal model of Ref. [26], which reproduces various experimental aspects of α-$RuCl_3$ [26,27,30,64,65] without hosting an in-plane field-induced QSL phase. In particular, it reproduces the magnetic-field dependence of the magnetotropic coefficient [65] recently reported [66,67]. We compute finite-temperature observables almost exactly [46] on a two-dimensional 24-site periodic cluster shown in the inset of Fig. 3. We stress that these calculations cannot capture features related to three-dimensional effects (like B_c^{AF1}), and finite-size effects lead to a smearing out of phase transitions. Nonetheless, this model and method capture the essential field- and temperature evolution of the anomalies at B_c^{AF2} and of the overall magnitude for the Grüneisen parameter (Fig. 3) and other measured quantities, as shown in the Supplemental

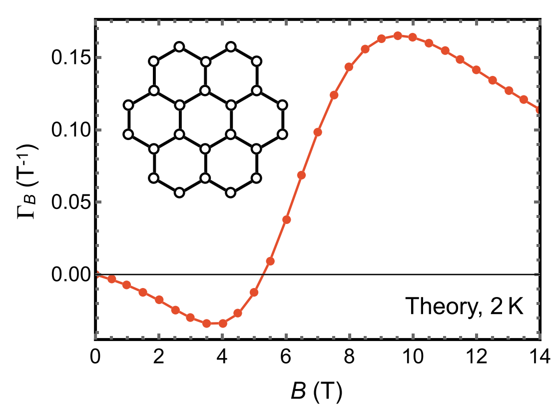

FIG. 3. $T = 2$ K exact diagonalization results of the magnetic Grüneisen parameter Γ_B for the minimal model of α-$RuCl_3$ [26]. The inset shows the employed periodic cluster.

Material [46]. Focusing now on Γ_B, we observe that the computed absolute order of magnitude as well as the sign change related to the suppression of zigzag order (B_c^{AF2}) at $B \approx 6$ T in the model agree well with experiment. In the partially polarized phase of the model ($B > 6$ T), Γ_B reaches its maximum not instantly at the phase transition, but at $B \approx 10$ T, which is likely related to the above mentioned finite-size effect. For all higher field strengths, Γ_B falls monotonically but stays positive.

The results provided by this model [26] however lack a shoulderlike anomaly like the one observed experimentally at B^*. On the other hand, since this shoulder lacks the appearance of a phase transition [59], we are led to ask, can anomalies occur in general Grüneisen parameters $\Gamma_\lambda \equiv -(\partial S/\partial \lambda)/C$ that are *not accompanied by phase transitions*? The universal zero-temperature limit of Γ_λ of all gapped phases is in fact markedly simple [46]:

$$\Gamma_\lambda(T \to 0) = \frac{\Delta'}{\Delta} \tag{1}$$

where Δ is the gap between the ground state and lowest excited state and $\Delta' \equiv d\Delta/d\lambda$. Equation (1) holds for both the magnetic Grüneisen parameter ($\lambda = B$) measured in this study, as well as the structural one ($\lambda =$ pressure).

From Eq. (1), we can anticipate two distinct types of anomalies in Γ_λ, which we illustrate via the schematic discrete spectrum shown in Fig. 4 (note that Eq. (1) nevertheless also holds for continuous spectra). If we consider a quantum phase transition at a critical λ_c, marked by a gap closure [68], it is easy to see that Γ_λ diverges [46] and changes sign from negative to positive upon closing ($\Delta' < 0$) and reopening ($\Delta' > 0$) of the gap. Provided the gap closes or opens as a power law in the thermodynamic limit, $\Delta \propto |\lambda - \lambda_c|^p$, a general consequence of this formula is that $\Gamma_\lambda \propto (\lambda - \lambda_c)^{-1}$ regardless of the specific power p. This recovers the known behavior for Grüneisen parameters at quantum critical points [59,60]. However, anomalies may also occur due to level crossings between the lowest excited states, which are labeled A and B in Fig. 4(a). While this crossing is comparatively invisible to the low-temperature specific heat C, the abrupt change in the slope of the gap (Δ') introduces a discontinuity in Γ_λ without a divergence as shown in Fig. 4(b) at λ^*. At small finite temperatures, the drop in Γ_λ is smeared out to a shoulderlike feature, that closely resembles B^* in experiment. In our interpretation, B^* therefore corresponds to an abrupt change in the nature of the lowest excitations, rather than to a phase transition.

Regarding α-$RuCl_3$, various scenarios may be consistent within this interpretation. The B^* anomaly may occur when the k point associated with the lowest energy excitations changes as a function of field within the partially polarized phase. While this does not occur in the minimal model [26] corresponding to Fig. 3, such an excited state level crossing is a recurring feature of models that are more proximate to a

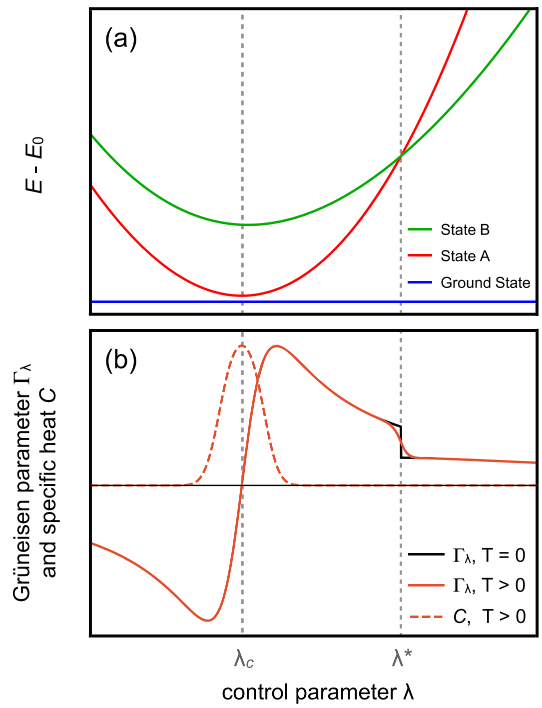

FIG. 4. (a) Schematic of a discrete spectrum evolving with a control parameter λ. It contains an avoided level crossing at λ_c and a level crossing in the lowest excited states at λ^*. These lead, respectively, to a sign change (λ_c) and a shoulder (λ^*) in the low-temperature Grüneisen parameter Γ_λ (b). If λ_c is a quantum critical point, the gap would vanish at λ_c in the thermodynamic limit, leading to a diverging Γ_λ at λ_c [46,59,60]. The low-temperature specific heat C [dashed curve] is nearly unaffected by the level crossing at λ^*.

zero-field phase other than zigzag AF. For example, we have found [46] an anomaly in Γ_B for a more complete *ab initio* derived model [44] that is closer to ferromagnetic order at zero field, and includes additional interaction terms beyond those considered in the minimal model [26]. In this case, the lowest-energy excitations switch from the zigzag wave vector to $\mathbf{k} = 0$ above a particular field strength within the gapped partially polarized phase. Such a scenario can be verified via inelastic neutron scattering probes of the high-field dispersion of the magnetic excitations where a change or shift of the k point with the softest mode may be observed around B^* [46]. In a more exotic scenario, the level crossings between the lowest excited states can also be induced by pushing the models closer to QSL phases, which we demonstrate by tuning nearer towards a hidden AF Kitaev point [46,63]. In both cases, our results imply the remarkable observation that the measured anomaly at B^* may indicate that α-$RuCl_3$ is proximate to competing phases at finite fields, but *does not enter them*. This poses the question whether the thermal Hall conductivity could also change anomalously at these field strengths without necessitating a phase transition, implying that no topological QSL would be entered or exited.

In summary, we have performed detailed high-resolution measurements of the specific heat and magnetic Grüneisen parameter of α-$RuCl_3$ as a function of in-plane magnetic field. The observed two transitions at $B_c^{\mathrm{AF1}} = 6.6$ T and $B_c^{\mathrm{AF2}} = 7.4$ T are consistent with previous reports and correspond to a transition between two AF states (B_c^{AF1}) and to a transition from the second AF state to the quantum paramagnetic state (B_c^{AF2}). We also observe a third broad shoulder anomaly in Γ_B centered around $B^* = 10$ T, consistent with previous studies [18,42]. This anomaly is invisible in the specific heat and inconsistent with a bulk phase transition. Thus, the upper field limit of the claimed half-integer thermal Hall plateau, which probably appears in this field range [38], cannot be explained by a phase transition between a presumed Kitaev QSL and polarized phase. We instead propose an alternative origin of the high-field anomaly as a change of the lowest-energy excitations without a phase transition, and demonstrate numerically that this is compatible with realistic microscopic models of α-$RuCl_3$.

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