Field-induced phase transitions of the Kitaev material $\alpha$-RuCl$_3$ probed by thermal expansion and magnetostriction

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High-resolution thermal expansion and magnetostriction measurements were performed on single crystals of $\alpha$-RuCl$_3$ in magnetic fields applied parallel to the Ru-Ru bonds. The length changes were measured in the direction perpendicular to the honeycomb planes. Our data show clear thermodynamic characteristics for the field-induced phase transition at the critical field $\mu_0 H_{c1} = 7.8(2) \, \mathrm{T}$ where the antiferromagnetic zigzag order is suppressed. At higher fields, a kink in the magnetostriction coefficient signals an additional phase transition around $\mu_0 H_{c2} \approx 11 \, \mathrm{T}$. The extracted Grüneisen parameter shows typical hallmarks for quantum criticality near $H_{c1}$. We compare our experimental data with linear spin-wave calculations employing a minimal Kitaev-Heisenberg model in the semiclassical limit. Most of the salient features are in agreement with each other, however, the peculiar features in the high-field region above $H_{c1}$ cannot be accounted for in our modelling and hence suggest a genuine quantum nature. We construct a phase diagram for $\alpha$-RuCl$_3$ showing two low-temperature transitions induced by an in-plane field along the Ru-Ru bonds.

The search for realizations of topological quantum spin liquids (QSLs) has generated a tremendous excitement, for both fundamental reasons and potential applications, e.g., in quantum information processing [1]. QSLs are characterized by long-range entanglement, topological order and associated ground-state degeneracies, as well as fractionalized quasiparticles. Kitaev’s spin-1/2 model on the honeycomb lattice [2] is a paradigmatic example for a QSL because it uniquely combines exact solvability in terms of Majorana fermions and experimental relevance [3–6].

One of the prime candidates to realize Kitaev magnetism is the compound $\alpha$-RuCl$_3$: It is a $J_{\text{eff}} = 1/2$ Mott insulator with a layered structure of edge-sharing RuCl$_6$ octahedra arranged in a honeycomb lattice [7–14]. While $\alpha$-RuCl$_3$ displays magnetic long-range order (LRO) of so-called zigzag type, a moderate in-plane magnetic field suppresses LRO resulting in a quantum disordered state whose nature has been debated [15–17]. By now, the existence of a quantum spin-liquid regime in $\alpha$-RuCl$_3$ in a window of applied magnetic field is suggested by a number of experimental results, such as an excitation continuum in neutron scattering [18–20], in Raman scattering [21], as well as in ESR/THz absorption measurements [22, 23], and, most prominently, an approximately half-quantized thermal Hall conductivity [17, 24]. The latter has been associated with the presence of a chiral Majorana edge mode, characteristic of a Kitaev spin liquid in applied magnetic field [25, 26]. Theoretically, a field-induced spin liquid has been discussed for microscopic models relevant to $\alpha$-RuCl$_3$ [27–29].

However, the structure of the field–temperature phase diagram of $\alpha$-RuCl$_3$ is not settled: The experiments of Refs. 17, 20, and 24 suggest the existence of at least three low-temperature phases, i.e., a spin-liquid phase sandwiched between the zigzag and high-field phases. Yet clear-cut thermodynamic evidence for a transition between the spin-liquid and high-field phases is lacking, perhaps with the exception of a signature in the magnetocaloric effect [20]. Moreover, the spin-liquid signatures have not been traced to very low temperatures, hence they may as well represent a quantum critical regime instead of a stable phase.

In this paper, we report a thorough dilatometric study of $\alpha$-RuCl$_3$ in in-plane magnetic fields up to 14 T and temperatures down to 3 K. Thermal expansion and magnetostriction represent thermodynamic properties governed by magnetoelastic coupling, enabling us to study the nature of the different phase transitions and possible critical behavior. We confirm the field-induced suppression of LRO at a critical field of $\mu_0 H_{c1} = 7.8(2) \, \mathrm{T}$ and provide strong thermodynamic evidence for quantum critical behavior at $H_{c1}$ by analyzing the Grüneisen parameter. This is confirmed by magnetostriction data, which moreover displays signatures of an additional first-order transition around $\mu_0 H_{c2} \approx 11 \, \mathrm{T}$. A comparison of
our experimental data to semiclassical calculations in a minimal lattice model yields qualitative agreement for many features, but also hint at additional physics above $H_{c1}$ beyond semiclassics. On basis of our experimental data we conjecture a field–temperature phase diagram of $\alpha$-RuCl$_3$ (for in-plane fields along the Ru-Ru bonds) containing three low-temperature phases, with the second transition terminating at a critical endpoint.

**Experimental:** High-quality single crystals of $\alpha$-RuCl$_3$ with a thickness of $\sim 1$ mm were grown using a vapor-transport technique [6]. Angular-dependent magnetization was measured to orient the samples parallel to the Ru-Ru bonds, $H \parallel$ Ru-Ru [30, 31], i.e., the field direction where the additional ordered phase found in Ref. 32 is absent or very narrow. The linear thermal expansion (TE) and magnetostriction (MS) of $\alpha$-RuCl$_3$ were determined by using a custom-built capacitive dilatometer with a parallel-plate system consisting of two separately aligned condenser plates, which detect changes of the uniaxial sample length $\Delta L_i$. The sample is clamped between one of the plates and the frame of the dilatometer, and thus is exposed to a small force via the springs of the dilatometer. Thus, all TE and MS studies were performed on two different single crystals with a thickness of $\sim 1.0$ mm (sample 1) and $\sim 0.8$ mm (sample 2).

**Thermal expansion:** We analyze the linear TE coefficient along the $c^*$ direction

$$\alpha_{c^*} = \frac{\partial (\Delta L_{c^*}/L_{c^*}(300 \text{ K}))}{\partial T},$$

where $\Delta L_{c^*}$ is the measured length change along the $c^*$ direction, which is then normalized to the sample length at room temperature. Anomalies in $\alpha(T)$ typically correspond to phase transitions. Low-temperature results for $\alpha$-RuCl$_3$ are shown in Fig. 1(a). At zero field the sharp peak signifies a single phase transition at $T_N = 7.2(1)$ K. With increasing field the peak broadens, reduces in magnitude, and shifts to lower temperatures, until it disappears at $\mu_0 H_{c1} = 7.8(2)$ T. Given the agreement with other probes, we conclude that this peak captures the magnetic transition into the zigzag phase. It highlights that the low-$T$ contributions to $\alpha$ are primarily magnetic, and also underlines the excellent quality of our single crystals, with an ABC stacking of the hexagonal layers along $c^*$ (see Supplement [33] for higher temperatures). We note that TE data for $\alpha$-RuCl$_3$ at $H = 0$ have been reported before in Ref. 34.

The inset of Fig. 1(a) displays a magnified region of Fig. 1(a) for fields near and above $H_{c1}$. The low-$T$ linear thermal expansion shows a sign change close to the critical field $H_{c1}$: at $H_{c1}$ the TE coefficient is tiny up to about 8 K, indicating that the phonon contribution is small in this temperature regime. For fields of 11.2 T and 13 T, $\alpha_{c^*}(T)$ is positive and monotonic. In this high-field regime, the magnitude of $\alpha_{c^*}$ decreases with increasing field, consistent with an increasing magnetic excitation gap in the polarized high-field phase as observed by various methods, such as NMR and thermal conductivity [35, 36]. Interestingly, the data at 8 T are anomalous in that $\alpha_{c^*}$ shows non-monotonic $T$ dependence, suggesting the existence of a distinct intermediate-field region between the zigzag and high-field phases, as recently also observed by other techniques [17, 20, 24].

The linear TE coefficient is proportional to the derivative of the entropy with respect to uniaxial pressure,
Magnetostriction: Field-driven phase transitions can be efficiently studied in MS experiments, measuring the 

\[ \frac{\partial S}{\partial p} \] [33]. Therefore, vanishing \( \alpha_c \) near \( H_{c1} \) indicates a maximum of the magnetic contribution to the entropy, \( S_{mag} \), at the critical field. In fact, such an entropy accumulation is predicted to occur near a continuous quantum phase transition [37, 38], and can be quantified using the Grüneisen parameter, commonly defined as the ratio between the magnetic contributions to the volume TE coefficient and the specific heat,

\[ \Gamma_V = V_m \frac{\alpha_{mag}}{C_{p, mag}} = -\frac{\partial S_{mag}}{\partial p} \frac{T}{(\partial S_{mag}/\partial T)}, \] (2)

where \( V_m \) is the molar volume. \( \Gamma_V \) displays characteristic divergencies [37] upon approaching a pressure-driven quantum critical point (QCP), and both \( \Gamma_V \) and \( \alpha \) change sign near a QCP as a result of entropy accumulation in the quantum critical regime [38].

Upon applying this concept to \( \alpha\text{-RuCl}_3 \) two remarks are in order: (i) Its phase transition(s) can be driven by both field and pressure, therefore both the field and pressure derivatives of the entropy will display sign changes, making \( \Gamma_V \) a suitable probe to detect QCPs. (ii) For the qualitative analysis, we will use the linear \( c^* \)-axis (instead of volume) TE coefficient, as this is much larger compared to that along the other directions [34]. For both \( \alpha_c \) and \( C_p \) the phononic contribution is assumed to be field-independent and had to be determined and subtracted from the \( \alpha\text{-RuCl}_3 \) data. The phononic contribution to the heat capacity \( C_p(T) \) was determined by measuring the non-magnetic structural analogue compound \( \text{RhCl}_3 \) [33, 39]; for the phononic contribution of \( \alpha_c(T) \) we used the \( \alpha\text{-RuCl}_3 \) data at 7.75 T as an approximation (see also [33]).

The resulting Grüneisen parameter \( \Gamma_V \) is depicted in Figs. 1(b) and 2(a) as function of temperature and applied magnetic field \( H \parallel \) Ru-Ru bonds, respectively. For a more comprehensive data set we refer the reader to the supplement [33]. As function of field, \( \Gamma_V \) changes sign at \( H_{c1} \) as expected. For fields below \( H_{c1} \), \( \Gamma_V(H) \) displays a peak at the Néel temperature \( T_N(H) \), while becoming small at high \( T \), Fig. 1(b). Moreover, below \( H_{c1} \) and at low \( T \), \( \Gamma_V(H) \) has its largest magnitude close to \( H_{c1} \), Fig. 2(a). The low-field part thus appears consistent with quantum critical phenomenology [38], and the fact that \( \Gamma_V(T) \) does not change sign at a temperature \( T \gtrsim T_N \) implies a large fluctuation regime above the quasi-two-dimensional magnetic transition. Together, the data signifies a continuous quantum phase transition at \( H_{c1} \) – the same conclusion was reached earlier based on a detailed analysis of low-\( T \) specific-heat measurements [39].

The low-\( T \) data for \( \Gamma_V \) above \( H_{c1} \) are again anomalous, in that there is no appreciable field dependence in \( \Gamma_V(H) \) between 8 and 11 T. As a result, the behavior of \( \Gamma_V(H) \) around \( H_{c1} \) is rather asymmetric, Fig. 2(a). We note that \( \Gamma_V \) for fields of 13 T and above displays large error bars at low \( T \) because both \( \alpha_{c, mag} \) and \( C_{p, mag} \) become very small as the magnetic excitations are gapped out.

**Magnetostriiction**: Field-driven phase transitions can be efficiently studied in MS experiments, measuring the

![Diagram](image-url)
length change as function of the applied field at constant $T$. Results for the linear MS coefficient along $c^\ast$, 

$$\lambda_{c^\ast} = \frac{1}{L_{c^\ast}(300K)} \frac{\partial \Delta L_{c^\ast}(\mu_0 H)}{\partial (\mu_0 H)},$$

are displayed in Fig. 2(b). At $T = 2.4$ K the continuous transition at $H_{c1}$ causes a sharp peak in $\lambda_{c^\ast}$ at $\mu_0 H = 7.8(2)$ T, which broadens and shifts to lower fields upon increasing temperature, thus tracking $T_N(H)$. At 10 K, i.e., above $T_N$, $\lambda_{c^\ast}$ deviates from the linear field dependence, as expected for a usual paramagnet. This is again related to the large fluctuation regime reaching up to temperatures of the exchange couplings ($\sim 50$ K); we recall that $\alpha$-RuCl$_3$ has been characterized as a “Kitaev paramagnet” in this regime [18, 40].

A striking feature is seen in the low-$T$ MS data above $H_{c1}$: While there is no signature for a second continuous transition in $\lambda_{c^\ast}(H)$ at 2.4 K, it displays a clear kink at $H_{c2} \approx 11$ T, see inset of Fig. 2(b). Upon increasing the temperature, the kink position varies only weakly while the kink magnitude (i.e. the change in slope) decreases, with the kink disappearing for temperatures above 8 K. These observations indicate an additional first-order transition, terminating in a critical endpoint around 8 K; however, we cannot exclude $H_{c2}$ representing a sharp crossover. No clear hysteresis around $H_{c2}$ was detected in our studies, but we note that small, non-reproducible eddy currents limit the resolution for such effects in our setup.

Modelling: In order to rationalize the experimental findings, we have calculated the linear TE and MS coefficients as well as the heat capacity in a minimal lattice model. It consists of spins 1/2 subject to nearest-neighbor Heisenberg $J_1$, Kitaev $K_1$ and off-diagonal $\Gamma_1$ interactions as well as third-nearest-neighbor Heisenberg $J_2$ interactions and is solved using linear spin-wave theory; details can be found in the supplement [33]. Modelling $\alpha_{c^\ast}$ and $\lambda_{c^\ast}$ requires input on the pressure dependence of the individual coupling constants, which is presently not available from ab-initio studies. We hence make reasonable assumptions [33] which eventually enable us to reproduce salient features of the experimental results, both at low and high fields.

A sample result of the theory is in Fig. 2(a) which displays the field dependence of the calculated Grüneisen parameter $\Gamma_V$ at a fixed low $T$. The match at low fields is convincing, however, the anomalous asymmetry of the measured $\Gamma_V$ around $H_{c1}$ does not appear compatible with our semiclassical results. The same applies to the non-monotonic behavior for $\alpha_{c^\ast}$ at fields slightly above $H_{c1}$ and the kink in the MS. Together, this suggests that the physics above $H_{c1}$ cannot be fully understood in terms of a continuous field-induced opening of a spin gap, and hence supports the interpretation of the experimental data in terms of a novel quantum phase between $H_{c1}$ and $H_{c2}$.

Phase diagram: Finally, we construct a temperature-field phase diagram of $\alpha$-RuCl$_3$ for $H \parallel$ Ru-Ru bonds using our TE, MS, and specific heat results. The phase diagram, Fig. 2(c), shows three low-temperature phases: (I) the low-field phase with zigzag LRO terminating at $\mu_0 H_{c1} = 7.8(2)$ T, (II) an intermediate phase between $H_{c1}$ and $H_{c2}$, and (III) a partially polarized, gapped high-field phase above $H_{c2}$.

We speculate that the intermediate phase (II) represents a topological quantum spin liquid as claimed by thermal Hall effect studies [17, 24]. Such a phase is not symmetry-distinct from the high-field phase (III) and does not require to be bounded by a thermal phase transition, hence the first-order transition line at $H_{c2}$ can indeed terminate at a critical endpoint. However, we note that $H_{c2}$ may in principle also be related to a change in the character of the magnetic excitations as probed by Raman and THz spectroscopy where indications for magnon bound states have been reported [41, 42].

Summary: Our high-resolution thermal expansion and magnetostriction measurements of $\alpha$-RuCl$_3$ along the $c^\ast$ axis confirm the field-induced suppression of long-range order at a critical field of $\mu_0 H_{c1} = 7.8(2)$ T, applied parallel to the Ru-Ru bonds, and provide thermodynamic evidence for quantum critical behavior at $H_{c1}$ from an analysis of the Grüneisen parameter. A clear kink in the measured linear MS coefficient at $\mu_0 H_{c2} \approx 11$ T hints at an additional first-order phase transition, while an additional second-order phase transition above $H_{c2}$ can be ruled out. A comparison of our experimental data to calculations using a minimal lattice model, solved in the semiclassical limit via linear spin-wave theory, shows that the behavior at low fields appears well captured by semiclassical theory. In contrast, the regime between $H_{c1}$ and $H_{c2}$ is not explained by our minimal lattice model. While we cannot draw clear conclusions about the nature of the low-$T$ state at these intermediate fields, we speculate that this represents the topological quantum spin liquid suggested earlier [17, 24].

Our findings call for a more detailed experimental study of the magnetostriction (and related quantities) in $\alpha$-RuCl$_3$ for different in- and out-of-plane field directions. Further theoretical work is needed investigating possible field-driven transitions in and out of the Putative spin liquid in Kitaev-based models [43] and trying to understand the field dependence of TE and MS in the spin-liquid phase.

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[1] C. Nayak, S. H. Simon, A. Stern, M. Freedman, and S. Das Sarma, Rev. Mod. Phys. 80, 1083 (2008).
[2] A. Kitaev, Annals of Physics 321, 2 (2006).
[3] G. Jaccoli and G. Khaliullin, Phys. Rev. Lett. 102, 017205 (2009).
[4] J. Chaloupka, G. Jaccoli, and G. Khaliullin, Phys. Rev. Lett. 105, 027204 (2010).
[5] S. Trebst, arXiv:1701.07056 (2017).
[6] A. Banerjee, J. Yan, J. Knolle, C. A. Bridges, M. B. Stone, M. D. Lumsden, D. G. Mandrus, D. A. Tennant, R. Moessner, and S. E. Nagler, Science 356, 1055 (2017).
[7] K. W. Plumb, J. P. Clancy, L. J. Sandilands, V. V. Shankar, Y. F. Hu, K. S. Burch, H.-Y. Kee, and Y.-J. Kim, Phys. Rev. B 90, 041112(R) (2014).
[8] J. A. Sears, M. Songvilay, K. W. Plumb, J. P. Clancy, Y. Qiu, Y. Zhao, D. Parshall, and Y.-J. Kim, Phys. Rev. B 91, 144420 (2015).
[9] R. D. Johnson, S. C. Williams, A. A. Haggighirad, J. Singleton, V. Zapf, P. Manuel, I. I. Mazin, Y. Li, H. O. Jeschke, R. Valentí, and R. Coldea, Phys. Rev. B 92, 235119 (2015).
[10] M. Majumder, M. Schmidt, H. Rosner, A. A. Tsirlin, H. Yasuoka, and M. Baenitz, Phys. Rev. B 91, 180401(R) (2015).
[11] Y. Kubota, H. Tanaka, T. Ono, Y. Narumi, and K. Kindo, Phys. Rev. B 91, 094422 (2015).
[12] S. Sinn, C. H. Kim, B. H. Lee, K. D. Lee, C. J. Won, J. S. Oh, M. Han, Y. J. Chang, N. Hur, H. Sato, B.-G. Park, C. Kim, H.-D. Kim, and T. W. Noh, Sci. Rep. 6, 39544 (2016).
[13] M. Ziatdinov, A. Banerjee, A. Maksov, T. Berlijn, W. Zhou, H. B. Cao, J.-Q. Yan, C. A. Bridges, D. G. Mandrus, S. E. Nagler, A. P. Baddorf, and S. V. Kalinin, Nat. Commun. 7, 13774 (2016).
[14] D. Weber, L. M. Schoop, V. Duppel, J. M. Lippmann, J. Nuss, and B. V. Lhotsy, Nano Lett. 16, 3578 (2016).
[15] R. Yadav, N. A. Bogdanov, V. M. Katukuri, S. Nishimoto, J. van den Brink, and L. Hozoi, Sci. Rep. 6, 37925 (2016).
[16] I. A. Leahy, C. A. Pocs, P. E. Siegfried, D. Graf, S.-H. Do, K.-Y. Choi, B. Normand, and M. Lee, Phys. Rev. Lett. 118, 187203 (2017).
[17] Y. Kasahara, T. Ominishi, Y. Mizukami, O. Tanaka, S. Ma, K. Sugii, N. Kuriha, H. Tanaka, J. Nasu, Y. Motome, T. Shibatachi, and Y. Matsuda, Nature (London) 559, 227 (2018).
[18] S.-H. Do, S.-Y. Park, J. Yoshitake, J. Nasu, Y. Motome, Y. S. Kwon, D. T. Adroja, D. J. Voneshen, K. Kim, T.-H. Jang, J.-H. Park, K.-Y. Choi, and S. Ji, Nat. Phys. 113, 1079 (2017).
[19] A. Banerjee, P. Lampen-Kelley, J. Knolle, C. Bals, A. A. Aczel, B. Winn, Y. Liu, D. Pajerowski, J. Yan, C. Bridges, A. Savici, B. C. Chakoumakos, M. D. Lumsden, D. A. Tennant, R. Moessner, D. G. Mandrus, and S. E. Nagler, npj Quantum Matter 3, 8 (2018).
[20] C. Balz, P. Lampen-Kelley, A. Banerjee, J. Yan, Z. Lu, X. Hu, S. M. Yadav, Y. Takano, Y. Liu, D. A. Tennant, M. D. Lumsden, D. Mandrus, and S. E. Nagler, Phys. Rev. B 100, 060405(R) (2019).
[21] L. J. Sandilands, Y. Tian, K. W. Plumb, Y.-J. Kim, and K. S. Burch, Phys. Rev. Lett. 114, 147201 (2015).
[22] Z. Wang, S. Reschke, D. Hüvonen, S.-H. Do, K.-Y. Choi, M. Gesch, U. Nagel, T. Room, and A. Loidl, Phys. Rev. Lett. 119, 227202 (2017).
[23] C. Wellin, J. Zeisler, A. Alfonsov, A. U. B. Wolter, M. Roslova, A. Isaeva, T. Doert, M. Vojta, B. Büchner, and V. Kataev, Phys. Rev. B 98, 184408 (2018).
[24] T. Yokoi, S. Ma, Y. Kasahara, S. Kasahara, T. Shibatachi, N. Kuriha, H. Tanaka, J. Nasu, Y. Motome, C. Hickey, S. Trebst, and Y. Matsuda, arXiv:2001.01899 (2020).
[25] J. Cookmeyer and J. E. Moore, Phys. Rev. B 98, 060412(R) (2018).
[26] Y. Vinkler-Aviv and A. Rosch, Phys. Rev. X 8, 031032 (2018).
[27] Y.-F. Jiang, T. P. Devereaux, and H.-C. Jiang, Phys. Rev. B 100, 165123 (2019).
[28] J. S. Gordon, A. Catuneanu, E. S. Sørensen, and H.-Y. Kee, Nat. Commun. 10, 2470 (2019).
[29] D. A. S. Kaib, S. M. Winter, and R. Valentí, Phys. Rev. B 100, 144445 (2019).
[30] L. Janssen, E. C. Andrade, and M. Vojta, Phys. Rev. B 96, 064430 (2017).
[31] P. Lampen-Kelley, S. Rachel, J. Reuther, J.-Q. Yan, A. Banerjee, C. A. Bridges, H. B. Cao, S. E. Nagler, and D. Mandrus, Phys. Rev. B 98, 100403(R) (2018).
[32] P. Lampen-Kelley, L. Janssen, E. C. Andrade, S. Rachel, J.-Q. Yan, C. Balz, D. G. Mandrus, S. E. Nagler, and M. Vojta, arXiv:1807.06192 (2018).
[33] See Supplemental Material for more details about thermal expansion and Grüneisen results, specific heat investigations for $H \parallel$ Ru-Ru bonds, and the theoretical modelling.
[34] M. He, X. Wang, L. Wang, F. Hardy, T. Wolf, P. Adelmann, T. Brückel, Y. Su, and C. Meingast, J. Phys.: Condens. Matter 30, 385702 (2018).
[35] S.-H. Baek, S.-H. Do, K.-Y. Choi, Y. S. Kwon, A. U. B. Wolter, S. Nishimoto, J. van den Brink, and B. Büchner, Phys. Rev. Lett. 119, 037201 (2017).
[36] R. Hentrich, A. U. B. Wolter, X. Zotos, W. Brenig, D. Nowak, A. Isaeva, T. Doert, A. Banerjee, P. Lampen-Kelley, D. G. Mandrus, S. E. Nagler, and M. Vojta, arXiv:1807.06192 (2018).
[37] See Supplemental Material for more details about thermal expansion and Grüneisen results, specific heat investigations for $H \parallel$ Ru-Ru bonds, and the theoretical modelling.
mens, C. Faugeras, Y. Gallais, and K.-Y. Choi, arXiv:1910.00800 (2019).

[43] L. Janssen and M. Vojta, J. Phys.: Condens. Matter 31, 423002 (2019).
Supplemental Material:
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I. THERMAL EXPANSION OF $\alpha$-RuCl$_3$ UP TO ROOM TEMPERATURE

While the focus of our work is on the low-temperature regime, we have also performed measurements up to room temperature. In Fig. S1 the normalized linear thermal expansion (TE) measured along the $c^*$ direction,

$$\frac{\Delta L_{c^*}(T)}{L_{c^*}(300 \text{ K})} = \frac{L_{c^*}(T) - L_{c^*}(T_{\text{min}})}{L_{c^*}(300 \text{ K})}$$

(S1)

of $\alpha$-RuCl$_3$ is depicted for zero field as well as for some representative in-plane magnetic fields $\mu_0 H || $ Ru-Ru bonds. $T_{\text{min}} = 3.6 \text{ K}$ represents the minimum temperature at which $L$ was measured and thus our data are referred to, i.e., the TE is zero at $T_{\text{min}}$.

The zero-field $c^*$-axis thermal expansion is rather large, as expected for weakly bonded van-der-Waals materials, Fig. S1(a). Further, the overall TE is decreasing upon lowering temperatures, which is in line with an overall shrinking of the lattice constants compared to room temperature [1, 2]. Interestingly, a step-like feature is seen in our TE data at around $T_{s,c} = 137 \text{ K}$ upon cooling, clearly indicating a first-order structural transition. The transition is strongly hysteretic, with $T_{s,w} = 161 \text{ K}$ upon warming. It most likely corresponds to a change from a high-temperature monoclinic $C2/m$ structure to a low-temperature rhombohedral $R3$ structure [2]. Note that $T_{s,c}$ and thus also the hysteresis upon this transition strongly depend on the used temperature sweep rate.

Looking at the details at low temperatures in zero field, Fig. S1(b), the overall shrinking of the $c^*$-axis TE is followed by a broad minimum at $\sim 14 \text{ K}$ and a subsequent expansion of the $c^*$ axis down to lowest temperatures. Furthermore, a sharp kink is clearly discernable at the antiferromagnetic transition temperature $T_N = 7.2(1) \text{ K}$.

FIG. S1. (color online) Normalized thermal expansion of $\alpha$-RuCl$_3$ perpendicular to the ab plane, $\Delta L_{c^*}/L_{c^*}(300 \text{ K})$, as function of temperature for both zero and finite applied magnetic fields $H || $ Ru-Ru bonds: (a) full temperature interval up to 300 K, (b) low-temperature region up to 30 K.

While the TE for $T \gtrsim 100 \text{ K}$ is not to be particularly sensitive to the application of an in-plane magnetic field, the low-temperature TE changes dramatically up to the critical field $\mu_0 H_{c1} = 7.8(2) \text{ T}$ at which the kink signalling

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the antiferromagnetic transition is finally completely suppressed. For fields larger than $H_{c1}$ a positive TE is discernable. Overall, our TE data are in good agreement with x-ray diffraction and former zero-field TE experiments [2, 3], showing a rearrangement of the unit cell of $\alpha$-RuCl$_3$ both at the structural and antiferromagnetic phase transitions, and thus also a coupling of the lattice and spin degrees of freedom in our compound.

II. THERMAL EXPANSION AND GRÜNEISEN PARAMETER FOR DIFFERENT SAMPLES

Thermal expansion was measured on two different samples of $\alpha$-RuCl$_3$ with similar crystal dimensions ($\sim 1$ and $\sim 0.8$ mm in thickness). In this way, sample dependencies due to crystal imperfections were tested. The linear thermal expansion coefficient $\alpha_c(T)$ and the corresponding Grüneisen parameter $\Gamma_V(T)$ on sample 2 are shown in Fig. S2. This can be compared to the same observables obtained for sample 1, as shown in Fig. 1 of the main paper. The key features are identical, i.e., the sharp peak in $\alpha_c$ at the antiferromagnetic phase transition $T_N = 7.2(1)$ K, the sign change of $\alpha_c$ and $\Gamma_V(T)$ at the critical field $\mu_0 H_{c1} = 7.8(2)$ T, and the quantum critical signature in $\Gamma(T)$. The shallow maximum in $\alpha_c(T)$ at low temperatures and at 8 T, however, cannot be observed in sample 2. This is probably related to the reduced thickness of sample 2 leading to even smaller changes in the TE, being at the resolution limit of our experimental setup for these kind of 2D van-der-Waals materials. It should be noted, however, that the linear TE coefficient at low temperatures and fields $\mu_0 H = 8 - 9$ T is also slightly increased for sample 2, see inset of Fig. S2(a).

Figs. S3 and S4 show the field dependencies of $\alpha_{c,mag}$ and $\Gamma_V$ for sample 1 and 2, respectively, for different temperatures between 3.5 K and 10 K. We chose to show both quantities here, since their accuracy is rather different: While the error bar of $\alpha_{c,mag}(H)$ is mainly determined by the reproducibility of our setup and the uncertainty of the subtracted phononic background contribution to $\alpha_c$, the error of $\Gamma(V) = V_m \alpha_{c,mag}/C_{p,mag}$ is influenced by more factors. This can be seen in our data on both samples, where $\Gamma_V(H)$ displays a large scatter and large errors in the high-field regime above 11.2 T, where both quantities $\alpha_{c,mag}$ and $C_{p,mag}$ become small due to the spin excitation gap. Still, both data sets are in good agreement with each other, evidencing the sign change of the linear TE coefficient and of $\Gamma_V$ at the critical field $\mu_0 H_{c1}$. Also the anomalous asymmetric Grüneisen parameter for fields around the critical field and the small absolute values for fields just above $H_{c1}$ are fully reproduced on both samples. We note that Fig. 2(a) of the main paper displays $\Gamma_V(H)$ at 4 K for both samples and at 10 K for sample 1.

To check the sensitivity of the key features found in the Grüneisen parameter with respect to the choice of the subtracted phononic background, we also used the 14 T data in the gapped high-field state as an approximation for the phononic contribution at low temperature (not shown). Although the spin excitation gap is still not large enough to fully gap out magnetic excitations above $\sim 6$ K, the key features of the resulting Grüneisen parameter are robust.

III. HEAT CAPACITY OF $\alpha$-RuCl$_3$

Specific-heat measurements under applied magnetic fields up to 14 T were performed on the same single crystal used for the dilatometry measurements (sample 1). For the experiments a heat-pulse relaxation method...

FIG. S2. (color online) (a) Temperature dependence of the TE coefficient perpendicular to the $ab$ plane, $\alpha_c$, for sample 2 of $\alpha$-RuCl$_3$ for zero and applied magnetic fields $H \parallel$ Ru-Ru bonds. The inset shows a zoom of the data for fields close to the critical field $\mu_0 H_{c1} = 7.8(2)$ T. (b) Grüneisen parameter $\Gamma_V(T)$ of $\alpha$-RuCl$_3$ of sample 2 parallel to the Ru-Ru bonds.
was used in a Physical Properties Measurement System (PPMS, Quantum Design). Via angular dependent magnetization studies, optical microscopy, and the use of a vertical puck the sample was properly aligned to ensure that the magnetic field was applied parallel to the Ru-Ru bond direction. In order to obtain the intrinsic specific heat of α-RuCl₃, the temperature- and field-dependent addenda were subtracted from the measured specific-heat values in the sample measurements.

The specific-heat coefficient \(C_p/T\) as a function of temperature and magnetic field shown in Fig. S5 agrees with previous reports, with one magnetic transition at zero field at \(T_N = 7.1(1)\, \text{K}\) defined at the peak position of \(C_p/T\). A tiny shoulder around 13 K hints at a very small amount of stacking faults leading to a different transition temperature in our sample. For \(\mu_0H \geq 8\, \text{T}\) the peak and thus the magnetic long-range order disappears, as expected.

The magnetic contribution to \(C_p\) was calculated by subtracting the lattice contribution from the experimental \(C_p(T)\) data. Such phononic contribution was obtained from the non-magnetic structural analog compound RhCl₃ (in polycrystalline form), after scaling its experimental specific-heat curve by the Lindemann factor [4], which was found to be 1.000059. The extracted magnetic contribution to the specific-heat coefficient of α-RuCl₃ is shown on semi-logarithmic scale in the inset of Fig. S5.

**IV. LOW-TEMPERATURE THERMODYNAMICS OF THE HONEYCOMB-LATTICE \(J_1-K_1-\Gamma_1-J_3\) MODEL**

**A. \(J_1-K_1-\Gamma_1-J_3\) model**

For a theoretical description of the thermodynamic behavior of α-RuCl₃ we employ a minimal model containing nearest-neighbor Heisenberg \(J_1\), Kitaev \(K_1\), and off-diagonal \(\Gamma_1\) interaction as well as a third-
FIG. S5. (color online) Specific-heat coefficient $C_p/T$ of α-RuCl$_3$ as function of temperature for applied magnetic fields $H \parallel$ Ru-Ru bonds, together with $C_p$ data for RhCl$_3$ (black stars). The inset shows the magnetic contribution $C_{p,\text{mag}}/T$ on a semi-logarithmic scale.

The nearest-neighbor Heisenberg $J_3$ interaction [5] on a two-dimensional honeycomb lattice:

$$\mathcal{H} = \sum_{\langle ij \rangle} [J_1 \vec{S}_i \cdot \vec{S}_j + K_1 S_i^z S_j^z + \Gamma_1 (S_i^\alpha S_j^\alpha + S_i^\beta S_j^\beta)]$$

$$+ \sum_{\langle ij \rangle} J_3 S_i^\alpha S_j^\alpha.$$  \hspace{1cm} (S2)

Here, \{\alpha, \beta, \gamma\} = \{x, y, z\} on a nearest-neighbor bond, for example. The spin quantization axes point along the cubic axes of the RuCl$_6$ octahedra, such that the [111] direction is perpendicular to the honeycomb $ab$ plane (referred to as $e^*$ axis) and the in-plane [100] direction points along a Ru-Ru nearest-neighbor bond of the honeycomb lattice. The model displays a $C_3^*$ symmetry of combined threefold rotations in real and spin space; a possible trigonal distortion spoiling this symmetry is neglected. Additional off-diagonal couplings, dubbed $\Gamma'$, are symmetry-allowed but assumed to be negligible.

The values for the exchange couplings can be estimated from the $ab$ initio calculations [5]; however, we find better agreement with our experimental data by using a slightly adapted parameter set that has recently been suggested by comparing with neutron scattering data (at zero field) [6]:

$$(J_1, K_1, \Gamma_1, J_3) = (-0.1, -1.0, +0.5, +0.1) \times A,$$  \hspace{1cm} (S3)

where $A$ is a global energy scale of the order of a few meV.

We are interested in the behavior of this model in the presence of an external magnetic field, i.e., described by the Hamiltonian $\mathcal{H}' = \mathcal{H} - g\mu_B \sum_i \vec{H} \cdot \vec{S}_i$ with $\vec{H} \parallel$ [100]. Here, $g\mu_B \vec{S}'$ corresponds to the effective moment of the $J_{sh} = 1/2$ states in the crystal. Our actual calculation will be formally performed in the semiclassical limit of $S \to \infty$, setting $S = 1/2$ at the end.

### B. Linear thermal expansion and magnetostriction

We are interested in calculating changes of the sample length perpendicular to the $ab$ plane, i.e., our goal is to calculate the linear thermal expansion coefficient and the linear magnetostriction rather than their volumetric counterparts. Given the anisotropy of the α–RuCl$_3$ crystal and the high sensitivity of the magnetic couplings to its structure, it is therefore important to also distinguish uniaxial from hydrostatic pressure. Keeping this in mind, we begin our thermodynamic analysis by writing down the differential of the Helmholtz free energy

$$dF = -SdT + \int d^3 \sigma_{ij} d\eta_{ij} - g\mu_0 \mu_B M dH,$$  \hspace{1cm} (S4)

where $S$ denotes the entropy (not to be confused with the spin size), $\sigma_{ij}$ and $\eta_{ij}$ are respectively the stress and strain tensors [7], and $M$ is the uniform magnetization. The spatial integral goes over the volume of the undeformed crystal [8, 9].

Now, we may refine our description by taking the $C_3^*$ symmetry of α–RuCl$_3$ into account. Indeed, this property implies that, under homogeneous stress, the system has only two independent length changes, namely of $\ell_c$ along the $c^*$ axis and $\ell_\perp$ perpendicular to it. Furthermore, it guarantees that $\eta_{ij}$ becomes diagonal in a coordinate system which has one of its axes parallel to $c^*$. Thus, if we assume that stress is homogeneous throughout the sample, we may rewrite (S4) in a simpler form:

$$dF = -SdT + V \sigma_{ij} d\eta_{ij} - g\mu_0 \mu_B M dH,$$  \hspace{1cm} (S5)

where $V$ denotes the volume of the undeformed crystal, and we employ the shorthand notations $\eta_{ij} \equiv \eta_{ii}$ and $\sigma_{ij} \equiv \sigma_{ii}$. Each diagonal strain element $\eta_{ii}$ then encodes information about the elongation along the $i$-th principal axis, such that $d\eta_{ii} = d\ln \ell_i$ [8, 10]. In the following, we shall identify $i = 3$ with the $c^*$ direction.

Under these conditions, one can use Maxwell relations derived from the Gibbs potentials to find [7]:

$$\alpha = \left( \frac{\partial \ln \ell_c}{\partial T} \right)_{\sigma,H} = \frac{1}{V} \left( \frac{\partial \mathcal{S}}{\partial \sigma_c} \right)_{\sigma,T,H},$$

$$\lambda = \left( \frac{\partial \ln \ell_c}{\partial (\mu_0 H)} \right)_{\sigma,T} = \frac{\mu_B}{V} \left[ \frac{\partial (gM)}{\partial \sigma_c} \right]_{\sigma,T,H}.$$

The $\sigma'$ which appears on the right-hand side of both (S6) and (S7) serves as a reminder that all stresses but $\sigma_c$ are to be held constant in carrying out the derivatives.

However, because our model only describes interactions within a honeycomb plane, we have no means to calculate $\sigma_c$ and thus cannot compute the observables directly from (S6) and (S7). Instead, we must consider...
how uniaxial stress along $c^*$ affects the microscopic parameters $J$ contained in the Hamiltonian, so that
\[ \alpha = \frac{1}{V} \sum_{J} \frac{\partial S}{\partial J} \frac{\partial J}{\partial \sigma_c}, \quad \lambda = \frac{\mu B}{V} \sum_{J} \frac{\partial (gM)}{\partial J} \frac{\partial J}{\partial \sigma_c}. \] (S8)

Here, we consider $J \in \{J_1, K_1, \Gamma_1, J_3, g\}$.

### C. Pressure dependence of the model parameters

As the expressions in (S8) illustrate, the sensitivity of each microscopic parameter to stress plays a key role in determining $\alpha$ and $\lambda$. For small distortions we may evaluate $J$ as an expansion up to first order in $\sigma_c$
\[ J(\sigma_c) \approx J_0 \left[ 1 + n_J (\sigma_c - \sigma_{c0}) \right], \] (S9)
where $\sigma_{c0}$ represents ambient stress, and we have defined
\[ n_J := \frac{1}{J_0} \frac{\partial J}{\partial \sigma_c} \bigg|_{\sigma_c = \sigma_{c0}}. \] (S10)

A positive $n_J$ therefore means that the absolute value of $J$ increases in response to increasing tensile stress $\sigma_c$ (i.e., decreasing pressure).

We note that comprehensive ab-initio information on the stress or pressure dependence of the couplings is presently lacking; it will be complex as both bond lengths and bond angles depend on the pressure conditions. We therefore treat the several $n_J$ as free parameters in our model. At this level, specific values will be chosen based on purely phenomenological criteria, in an attempt to reproduce the main features of the experimental results in regimes where spin-wave theory is reliable.

### D. Spin-wave theory

Having established a connection between stress along the $c^*$ axis and the magnetic properties of the system, we now compute the Helmholtz free energy in order to complete our thermodynamic analysis. In the following, we outline how to do so by using linear spin-wave theory (LSWT). This non-interacting-boson approach is expected to provide reliable results at low temperatures in both the ordered and the polarized high-field phases where the number of magnon excitations is small. It is, however, not reliable (i) at low fields for temperatures comparable to or above the Néel temperature and (ii) at high fields for temperatures comparable to or above the spin gap. This includes the quantum critical regime near $H_{c1}$.

As a starting point for LSWT, one must select a classical spin configuration that minimizes $\mathcal{H}$. This problem has already been addressed in a previous study involving the same conditions we consider here [11]. As a result, it was shown that the Hamiltonian (S2) hosts three different zigzag patterns as degenerate classical ground states. However, such a degeneracy is lifted by a $[110]$ field, which selects the configuration with zigzag chains running perpendicularly to it. This happens because the corresponding zero-field order is normal to the $b$ axis, so that the spins cant uniformly in response to the magnetic field [12]. Canting increases until the critical field, $H_{c1}$, is reached and a continuous transition from the canted zigzag to a polarized state takes place.

Next, we employ a standard procedure involving the Holstein-Primakoff transformation, whereby quantum fluctuations with respect to a given reference state are described as magnonic excitations [13–15]. We thus introduce the bosonic modes $\{a_{i\nu}^\dagger, a_{i\nu}\}$, where $a_{i\nu}^\dagger$ and $a_{i\nu}$ are the magnon creation and annihilation operators at site $\nu$ in the magnetic unit cell $i$. The index $\nu$ runs from 1 to the number of magnetic sublattices, $N_\nu$, so that $N_\nu = 2$ and 4 in the polarized and canted zigzag phases, respectively.

Hence, by only keeping the terms up to next-to-leading order in $1/S$ and taking a Fourier transform, we arrive at a quadratic spin-wave Hamiltonian
\[ \mathcal{H}_{SW} = N \epsilon_{cl} + \frac{1}{2} \sum_k \left( \Psi_k^\dagger M_k \Psi_k - \text{Tr} \, \hat{A}_k \right), \] (S11)
where $N$ is the total number of sites, $\epsilon_{cl}$ is the classical energy per site and $\Psi_k = \left(a_{k1}^\dagger \ldots a_{kN_\nu}^\dagger, a_{-k1} \ldots a_{-kN_\nu}\right)$. One can show that the $2N_\nu \times 2N_\nu$ matrix $M_k$ may generically be written in terms of two $N_\nu \times N_\nu$ submatrices, $\hat{A}_k$ and $\hat{B}_k$, as
\[ M_k = \left( \begin{array}{cc} \hat{A}_k & \hat{B}_k \\ \hat{B}_k^T & \hat{A}_k^T \end{array} \right), \] (S12)
$\mathcal{H}_{SW}$ can then be diagonalized via a Bogoliubov transformation, from which we obtain the eigenenergies $\epsilon_{k\nu}$. While this step was performed analytically in the polarized phase, it required a numerical approach for $H < H_{c1}$.

In these terms, we may write the Helmholtz free energy for a system of non-interacting bosons as
\[ F = E_{gs} + k_B T \sum_{k\nu} \ln \left( 1 - e^{-\beta \epsilon_{k\nu}} \right), \] (S13)
where $\beta^{-1} = k_B T$ and
\[ E_{gs} = N \epsilon_{cl} + \frac{1}{2} \sum_k \left( \sum_{\nu=1}^{N_\nu} \epsilon_{k\nu} - \text{Tr} \, \hat{A}_k \right) \] (S14)
denotes the ground-state energy including the leading order corrections in $1/S$. Then, by combining (S8) and (S13), we find
\[ \alpha = -\frac{1}{k_B T^2 V} \sum_J n_J \sum_{k\nu} \frac{e^{\beta \epsilon_{k\nu}} \epsilon_{k\nu}}{(e^{\beta \epsilon_{k\nu}} - 1)^2} \frac{\partial \epsilon_{k\nu}}{\partial J} \] (S15)
and
\[ \lambda = -\sum_{\mathcal{J}} \frac{J_0 n_{\mathcal{J}}}{\mu_0 V} \left\{ N \frac{\partial^2}{\partial J \partial H} \left( \epsilon_{cl} - \frac{\text{Tr} \mathbb{A}_k}{2N_s} \right) \right\} + \sum_{\mathbf{k}^\nu} \left[ \left( \frac{1}{2} + \frac{1}{e^{\beta \epsilon_{cl}} - 1} \right) \frac{\partial^2 \epsilon_{k^\nu}}{\partial J \partial H} - \frac{\beta e^{\beta \epsilon_{k^\nu}}}{(e^{\beta \epsilon_{k^\nu}} - 1)^2} \frac{\partial \epsilon_{k^\nu}}{\partial H} \frac{\partial \epsilon_{k^\nu}}{\partial J} \right] \right\}. \]  

(S16)

Note that, in order to get (S16), we have used the fact that \( \text{Tr} \mathbb{A}_k \) is momentum-independent for the phases we consider here. Another noteworthy point is that both \( \alpha \) and \( \lambda \) are given as a linear combination of terms which result from varying one microscopic parameter at a time. While this does not hold beyond the approximation (S9), it allowed us to analyze an arbitrarily wide range of sets \( \{n_{\mathcal{J}}\} \) without demanding extra computational time.

A third quantity of interest is the magnetic heat capacity at constant strain

\[ C_\eta (T, H) = \frac{1}{k_B T^2} \sum_{\mathbf{k}^\nu} \left( e^{\beta \epsilon_{k^\nu}} - 1 \right)^2. \]  

(S17)

In the following, we will compare \( \alpha/C_\eta \) to the Gr"uneisen parameter measured in the experiments, even though both observables are not strictly equal. That is because the Gr"uneisen parameter is defined as the ratio between the thermal expansion coefficient and the heat capacity at constant stress rather than constant strain. Still, we shall refer to \( \alpha/C_\eta \) as the Gr"uneisen parameter from now on for simplicity.

### E. Results

In the following, we will compare \( \alpha/C_\eta \) to the Gr"uneisen parameter measured in the experiments, even though both observables are not strictly equal. That is because the Gr"uneisen parameter is defined as the ratio between the thermal expansion coefficient and the heat capacity at constant stress rather than constant strain. Still, we shall refer to \( \alpha/C_\eta \) as the Gr"uneisen parameter from now on for simplicity.

#### 1. Thermal expansion

Let us begin by discussing our thermal expansion results, which are shown in the top row of Fig. S6. After a brief inspection of these plots, one can see that both sets of coefficients presented in Table S1 reproduce gross features of the experimental data, such as: (i) \( \alpha \) is negative for \( H < H_{c1} \) and positive for \( H > H_{c1} \); (ii) the magnitude of \( \alpha \) is markedly smaller for \( \mu_0 H \gtrsim 11 \) T than for \( \mu_0 H \lesssim 7 \) T; (iii) \( \alpha \) is suppressed by increasing \( H \) at sufficiently high fields. Moreover, set 1 also leads to the correct field trend in the zigzag phase, whereby the magnitude of \( \alpha \) becomes larger as one increases \( H \) at a fixed temperature. On the other hand, set 2 only does so approximately, since the trend is spoiled near zero field. We recall that LSWT does not capture the thermal phase transition at \( T_N \), hence a corresponding peak in \( \alpha(T) \) is missing, and a comparison of experiment and theory should be restricted to \( T < T_N \).

Upon analyzing different combinations of the coefficients \( n_{\mathcal{J}} \), we were unable to obtain a reasonable agreement with experiment without considering a positive and considerably large \( n_{J_3} \). This interesting observation suggests that uniaxial pressure along the \( c^* \) axis destabilizes the zigzag phase, since this particular type of magnetic ordering is favored by a positive \( J_3 \).

As an additional remark on the role of the coefficients \( n_{\mathcal{J}} \), we point out that the correct field evolution for \( H < H_{c1} \) requires a large and positive \( n_{r_1} \). Increasing \( n_{K_1} \) and \( n_{J_1} \) tends to cancel this trend and even produce negative values for \( \alpha \) in the polarized phase at temperatures larger than 15 K.

| \( n_{J_1}/n_{r_1} \) | \( n_{K_1}/n_{r_1} \) | \( n_{J_3}/n_{r_1} \) | \( n_{K_3}/n_{r_1} \) | \( n_{g}/n_{r_1} \) |
|---|---|---|---|---|
| Set 1 | 0.3 | 0.3 | 1.6 | 0.0 |
| Set 2 | 0.5 | 0.75 | 0.56 | -0.65 |

TABLE S1. Different sets of parameters \( n_{\mathcal{J}} \) describing the pressure dependence of the couplings according to Eq. (S10). \( n_{r_1} \) is used as reference scale, see text.
FIG. S6. (color online) From top to bottom: thermal expansion coefficient, Grüneisen parameter and magnetostriction plots for the two sets of microscopic parameters given in Table S1. In the plots where the independent variable is the magnetic field, the vertical gridline represents the critical field, $\mu_0 H_{c1} = 7.8$ T. In all panels, the left vertical axis gives the theory result normalized to $n_{\Gamma_1}$, the right vertical axis shows experimental units using $n_{\Gamma_1} = 0.9$ GPa$^{-1}$ and $V/N = 92.8$ Å$^3$ [1, 2, 18]. Our semiclassical analysis does not show any of the features interpreted as signatures of a novel phase at intermediate fields above $H_{c1}$ and thus supports its genuine quantum character.

With that said, we emphasize that neither sets 1, 2, nor any other combination of coefficients we considered in our analysis produces the non-monotonic behavior for $\alpha(T)$ at fields slightly above $H_{c1}$, as reported in experiment. Instead, we generally find that $\alpha$ increases monotonically at a fixed temperature as $H \to H_{c1}^+$. Next, we can discuss the evolution of the Grüneisen parameter as a function of the magnetic field (see the second row of plots in Fig. S6). Our results show the correct signs above and below $H_{c1}$, as we have enforced this by a careful analysis of the thermal expansion data. Very close to $H_{c1}$ magnon excitations proliferate and the non-interacting boson picture underlying LSWT becomes inadequate. Hence, the evolution of $\alpha$ and $\alpha/C_\eta$ through the critical field cannot be reliably computed in our approach. On general grounds [17] we expect that...
both quantities evolve smoothly at fixed finite $T$ as function of $H$, with the exception of a singularity at $T_N(H)$, crossing zero near $H_{c1}$. 

As noted above, we expect our calculations to yield correct results at sufficiently high fields and low temperatures, where the magnon excitation gap is comparable to or larger than $k_BT$. Based on this premise, we stress that our theoretical data cannot produce an asymmetric, anomalous behavior for the Grüniesen parameter at low $T$ above the critical field. This is also illustrated in Fig. 2(a) of the main text where theory results for $\Gamma_V(H)$ at a temperature of 4 K are shown vis-a-vis the experimental data; we note that the portion of the theory curve where LSWT is unreliable has been removed there.

2. Magnetostriction

When we move to the results on the magnetostriction (bottom row of Fig. S6), we see that both sets of coefficients correctly produce negative values of $\lambda$ for the whole range of magnetic fields considered here. However, set 1 notably leads to large non-monotonic variations around an inflection point in the zigzag phase which are not observed in experiment. The origin of this is in the behavior of the magnon spectrum which evolves in a highly non-trivial fashion with field.

When trying to reduce the intensity of this feature in $\lambda$, we verified that it becomes even larger if one, for instance, decreases $n_{K_1}$. In fact, without considering variations in $g$, we were unable to find a parameter set capable of smoothing out such a contortion while preserving the main characteristic from the thermal expansion coefficient. As far as we could check, this is only accomplished by taking $n_g < 0$, which motivated us to consider the second set of coefficients.

We recall that LSWT does not produce critical behavior at $T_N$, therefore $\lambda(H)$ displays a singularity at $H_{c1}$ for all temperatures, instead of a singularity at $T_N(H)$ (or the corresponding Néel field $H_N(T)$).

In regard to the behavior for $H > H_{c1}$, our results do not bear any resemblance to the kink found in experiment. Together with the absence of a non-monotonic behavior in $\alpha$ around 8 T and the lack of the asymmetric, anomalous Grüniesen parameter above $H_{c1}$, this supports the interpretation of the experimental data in terms of evidence for a novel phase directly above $H_{c1}$, since all of these features are incompatible with our semiclassical treatment.

[1] R. D. Johnson, S. C. Williams, A. A. Haghighirad, J. Singleton, V. Zapf, P. Manuel, I. I. Mazin, Y. Li, H. O. Jeschke, R. Valenti, and R. Coldea, Phys. Rev. B 92, 235119 (2015).
[2] S.-Y. Park, S.-H. Do, K.-Y. Choi, D. Jang, T.-H. Jang, J. Schefer, C.-M. Wu, J. S. Gardner, J. M. S. Park, J.-H. Park, and S. Ji, arXiv:1609.05690.
[3] M. He, X. Wang, L. Wang, F. Hardy, T. Wolf, P. Adelmann, T. Bräckel, Y. Su, and C. Meingast, J. Phys.: Condens. Matter 30, 385702 (2018).
[4] F. A. Lindemann, Phys. Z. 11, 609 (1910).
[5] S. M. Winter, Y. Li, H. O. Jeschke, and R. Valenti, Phys. Rev. B 93, 214431 (2016).
[6] S. M. Winter, K. Riedl, A. Honecker, and R. Valenti, Nat. Commun. 8, 1152 (2017).
[7] We note that, according to standard sign conventions [9], positive stress leads to an elongation (i.e. to positive strain) along a given axis. Thus, stress and uniaxial pressure have opposite signs.
[8] L. D. Landau and E. M. Lifshitz, Course of Theoretical Physics Vol 7: Theory and Elasticity. Pergamon Press (1959).
[9] P. M. Chaikin and T. C. Lubensky, Principles of Condensed Matter Physics, Cambridge University Press (2000).
[10] G. D. Barrera, J. A. O. Bruno, T. H. K. Barron and N. L. Allan, J. Phys.: Condens. Matter 17 (2005).
[11] L. Janssen, E. C. Andrade, and M. Vojta, Phys. Rev. B 96, 064430 (2017).
[12] L. Janssen and M. Vojta, J. Phys. Condens. Matter 31, 423002 (2019).
[13] T. Holstein and H. Primakoff, Phys. Rev. 58, 1098 (1940).
[14] J. P. Blaizot and G. Ripka, Quantum Theory of Finite Systems, MIT Press, 1986.
[15] J. Rau, P. A. McClarty and R. Moessner, Phys. Rev. Lett. 121, 237201 (2018).
[16] R. Yadav et al., Phys. Rev. B 98, 121107(R) (2018).
[17] M. Garst and A. Rosch, Phys. Rev. B 72, 205129 (2005).
[18] H. B. Cao, A. Banerjee, J.-Q. Yan, C. A. Bridges, M. D. Lumsden, D. G. Mandrus, D. A. Tennant, B. C. Chakoumakos, and S. E. Nagler, Phys. Rev. B 93, 134423 (2016).