Supplemental Material: Strong effects of uniaxial pressure and short-range correlations in $Cr_2Ge_2Te_6$

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In the following

- the crystal structure
- specific heat data and its background subtraction for $Cr_2Ge_2Te_6$ and the non-magnetic analog $In_2Ge_2Te_6$
- the thermal expansion coefficients at 0 and 15 T
- effective magnetic Grüneisen parameters
- high temperature magnetostriction data

are shown supporting the results of our manuscript.

I. CRYSTAL STRUCTURE

The crystal structure of $Cr_2Ge_2Te_6$ is shown in Fig. S1.

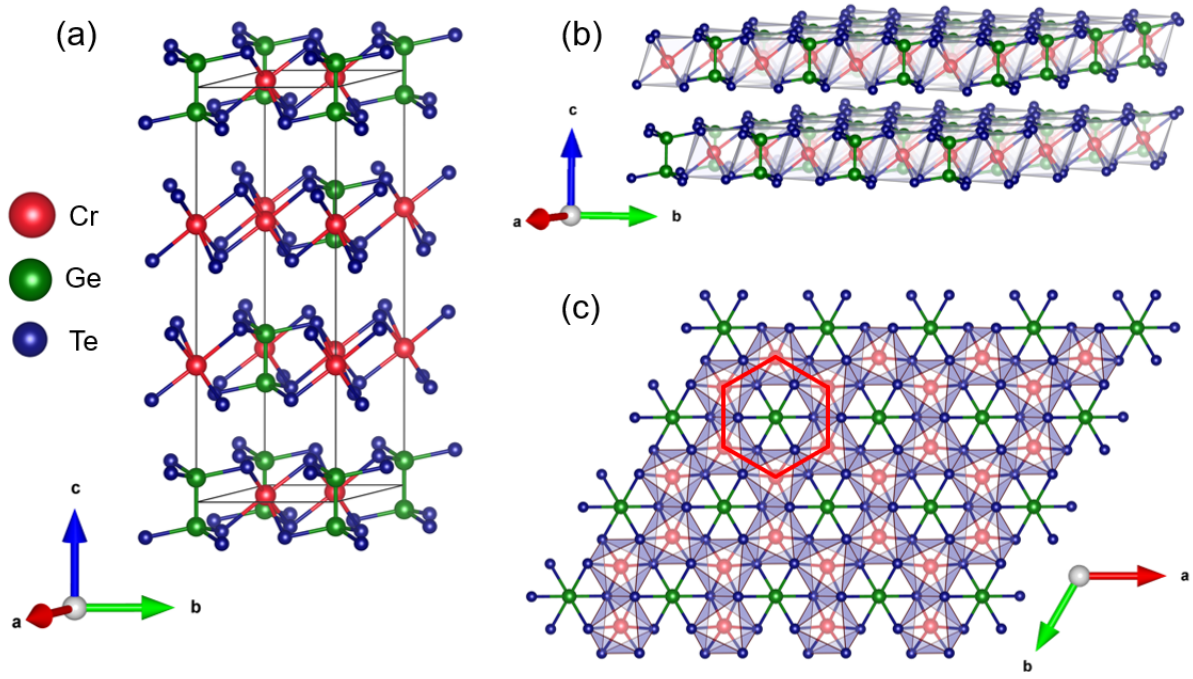

Figure S1. Crystal structure of $Cr_2Ge_2Te_6$ in the space group $R\bar{3}$ (no. 148) as reported in Ref. [1]. (a) Unit cell of $Cr_2Ge_2Te_6$. (b) Van der Waals layers and stacking along the c axis with Cr octahedra shown. (c) View onto the ab plane with one unit of the honeycomb network indicated by the red hexagon.

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II. SPECIFIC HEAT DATA

As explained in the main text, the thermal expansion data (Fig. 2) suggest – without any assumption about phonon-backgrounds or the like – that short-range correlations in $Cr_2Ge_2Te_6$ extend to at least 200 K. This makes a reliable background correction difficult since the extent of the anomaly in T_C can not be determined easily. Any phononic background fit to the specific heat or thermal expansion coefficient of $Cr_2Ge_2Te_6$ will thus contain a large uncertainty. Trying to improve the uncertainty of a background fit, we measured the specific heat of $In_2Ge_2Te_6$, a non-magnetic analog to $Cr_2Ge_2Te_6$(Fig. S2(a)). The background fitting procedure to $In_2Ge_2Te_6$ and $Cr_2Ge_2Te_6$ is described in the following.

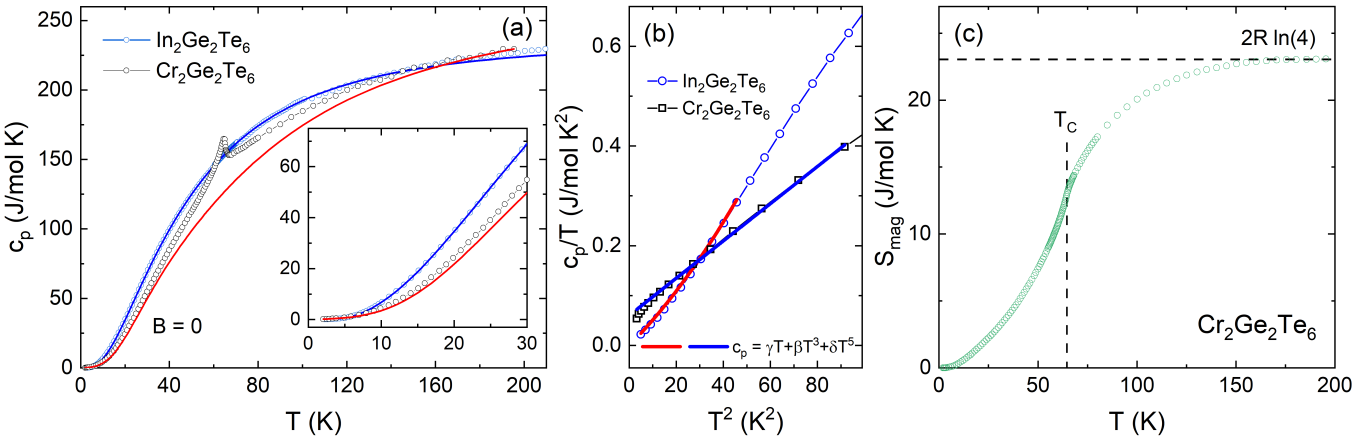

Figure S2. (a) Specific heat c_p of $In_2Ge_2Te_6$ (blue open circles) and $Cr_2Ge_2Te_6$ (black open circles) with a fits of Debye and Einstein modes (solid lines) as explained in the text. Inset: magnification of the low temperature regime. (b) Specific heat c_p/T vs. T^2 of $In_2Ge_2Te_6$ (blue open circles) and $Cr_2Ge_2Te_6$ (black open squares) at low temperatures. Lines in (b) indicate fits to obtain γ_{el} and β (see text). (c) Magnetic entropy of $Cr_2Ge_2Te_6$ calculated after the phononic background subtraction from c_p. The horizontal dashed line indicates the theoretically expected magnetic entropy for a spin-$\frac{3}{2}$ system. T_C is indicated by the vertical dashed line.

In principle, separating out the phononic and electronic contributions from the specific heat of such an analog should enable determining the excess specific heat, i.e., the magnetic contributions, of the magnetic compound. The phonon part of the specific heat can usually be modeled well with a combination of Debye and Einstein modes:

$$c_{V,ph} = \sum_i c^D_{V,ph,i} + \sum_j c^E_{V,ph,j} \tag{1}$$

with the Debye part given as

$$c^D_{V,ph,i} = 9 \cdot n_{D,i} \cdot k_B \left(\frac{T}{\Theta_{D,i}}\right)^3 \cdot \int_0^{\Theta_{D,i}/T} \frac{x^4 e^x}{(e^x-1)^2} dx \tag{2}$$

and the Einstein part given by

$$c^E_{V,ph,j} = 3 \cdot n_{E,j} \cdot k_B \left(\frac{\Theta_{E,j}}{T}\right)^2 \cdot \frac{e^{\Theta_{E,j}/T}}{[e^{\Theta_{E,j}/T}-1]^2} \quad . \tag{3}$$

At sufficiently low temperatures the measured specific heat at constant pressure, c_p, is approximately the same as the specific heat at constant volume, c_V,

$$c_p \approx c_V \quad . \tag{4}$$

The difference between c_p and c_V is given by,

$$c_p - c_V = TVB\beta^2 \tag{5}$$

with a molar volume $V = V_m = 1.67 \times 10^{-4}$ m^3/mol, the volume expansion $\beta \propto 10^{-5}$/K and the bulk modulus $B \approx 14$ GPa ($Cr_2Ge_2Te_6$, see Ref. 2), such that

$$c_p - c_V < 0.1 \text{ J/(mol K) @300 K.} \tag{6}$$

Deviations between c_p and c_V are thus roughly on the order of 0.1 J/(mol K) around room temperature and even smaller as the temperature is decreased.

A. Low Temperature Fits

For an estimate of (1) the (linear) electronic contribution to the specific heat as well as (2) the Debye temperature we performed a low-temperature fit (Fig. S2(b)). For this fit we used the formula

$$c_p = \gamma T + \beta T^3 + \delta T^5 \tag{7}$$

where $\gamma = \gamma_{el}$ is the Sommerfeld coefficient and β and δ are low temperature lattice contributions to the specific heat. β can be used to calculate an estimate of the Debye temperature by

$$\Theta_D = \left(\frac{12\pi^4 nR}{5\beta}\right)^{1/3} \tag{8}$$

with R being the molar gas constant and n the number of atoms per formula unit.

Fitting the specific heat of $In_2Ge_2Te_6$ in the temperature range from 2 K to 7 K (Fig. S2(b)) we obtained $\gamma = 0$, $\beta = 4.72$ mJ/(mol K^4) and $\delta = 36.6$ μJ/(mol K^6). From β we then obtained $\Theta_D = 160.3$ K. A fit in the range from 2 K to 10 K yielded $\gamma = 0$, $\beta = 5.74$ mJ/(mol K^4) ($\Theta_D = 150.2$ K) and $\delta = 11.7$ μJ/(mol K^6), but with a worse agreement to the data at low temperatures.

A fit to the $Cr_2Ge_2Te_6$ specific heat from 1.8 K to 10.5 K yielded $\gamma = 62(5)$ mJ/(mol K^2), $\beta = 3.66$ mJ/(mol K^4) ($\Theta_D = 174.5$ K) and $\delta = 0$. For comparison, at fit from 1.8 K to 14.5 K yielded $\gamma = 91(8)$ mJ/(mol K^2), $\beta = 3.23$ mJ/(mol K^4) ($\Theta_D = 181.9$ K) and also $\delta = 0$, but with a worse fit quality.

From these low-temperature fits we adopted the Sommerfeld coefficients $\gamma_{el} = 0$ for $In_2Ge_2Te_6$ and $\gamma_{el} = 60$ mJ/(mol K^2) for $Cr_2Ge_2Te_6$ for the fitting up to high temperatures which is shown in the next sections.

B. $In_2Ge_2Te_6$ High Temperature Fitting

The $In_2Ge_2Te_6$ specific heat data in Fig. S2(a) shows a minor step around 102 K, indicating a small negative offset of all data points above 102 K, probably from a slight decoupling of the sample from the calorimeter. Therefore, the data was only fitted in the range from 2 K to 100 K. The Best fit was achieved using two Debye modes (Eq. (2)) and one Einstein mode (Eq. (3)) with $\Theta_{D,1} = 134.4$ K, $n_{D,1} = 4.58$, $\Theta_{D,2} = 286.5$ K, $n_{D,2} = 4.47$, $\Theta_E = 44.5$ K and $n_E = 0.459$. The sum over the weights n_i is 9.51, close to the expected value of 10 for 10 atoms per formula unit. As seen in Fig. S2(a) and (b) this fit describes both the low-temperature and the high temperature ranges very well.

C. $Cr_2Ge_2Te_6$ High Temperature Fitting

Bouvier et al. [3] suggested a simple scaling of the specific heat data of two ternary compounds by the ratio of their Debye temperatures. However, this scaling is only valid for low temperatures, up to roughly $T \lesssim \Theta_D/10$. Accordingly, the specific heat of $Cr_2Ge_2Te_6$ crosses the specific heat of $In_2Ge_2Te_6$ around 120 K and it is obvious that such a simple scaling by $\Theta_{D,IGT}/\Theta_{D,CGT} = 0.952$ fails. The intended $Cr_2Ge_2Te_6$ background subtraction by the non-magnetic analog $In_2Ge_2Te_6$ is thus not possible. Instead, we tried several combinations of Debye and Einstein modes before we ended up with the combination of two Debye modes with fixed $\gamma = 60$ mJ/(mol K^2) as described in the main text. For fits with the different combinations of Debye and Einstein modes, the resulting Debye and Einstein temperatures strongly depend on the applied fitting range and vary roughly around 60 K $< \Theta_{D,1} <$ 200 K and 250 K $< \Theta_{D,2} <$ 400 K. The Debye temperatures of $In_2Ge_2Te_6$ together with the three assumptions mentioned in the main text served as a starting point to arrive at the final values. For these final values the Debye temperatures and weights $n_{D,i}$ were incrementally changed to achieve (1) a total magnetic entropy in line with a spin-$\frac{3}{2}$ system, i.e., $S_{\mathrm{mag}} \approx S_{\mathrm{mag,theo}} = 2Rln(4) = 23.05$ J/(mol K) (with two moles of Cr atoms per mole of $Cr_2Ge_2Te_6$, and R being the molar gas constant), (2) a peak shape of $c_{p,\mathrm{mag}}$ resembling that of the thermal expansion coefficient and (3) a magnetic entropy vanishing around 200 K as indicated by the plateau in α_c (Fig. 2(a)). The final best fit values we arrived at were $\Theta_{D,1} = 150$ K, $n_{D,1} = 4.8$, $\Theta_{D,2} = 410$ K, and $n_{D,2} = 5.024$.

The magnetic entropy resulting after subtraction of the phononic and electronic fit is shown in Fig. S2(c).

Note that both the $In_2Ge_2Te_6$ and the $Cr_2Ge_2Te_6$ data do not reach the expected classical Dulong-Petit limit of $c_p = 3nR \approx 249.4$ J/(mol K) at high temperatures, where n is the number of atoms per formula unit and R is

the molar gas constant. The $In_2Ge_2Te_6$ data reach 233 J/(mol K) at 230 K and the $Cr_2Ge_2Te_6$ data reach about 230 J/(mol K) at 195 K, with both curves still increasing. Looking at $\sum_i n_i$ from the fit results, the experimental error can thus be estimated to amount to about 5% for $In_2Ge_2Te_6$ and about 2% for $Cr_2Ge_2Te_6$.

III. THERMAL EXPANSION COEFFICIENTS AT 0 AND 15 T

The thermal expansion coefficients derived from the relative length changes in Fig. 1 in the main text are presented in Fig. S3. The effective Grüneisen parameter $\gamma_{c,\mathrm{eff}} = 7.0 \times 10^{-8}$ is slightly different from the one extracted from the mini-dilatometer in Fig. 2(a) (8.05×10^{-8}).

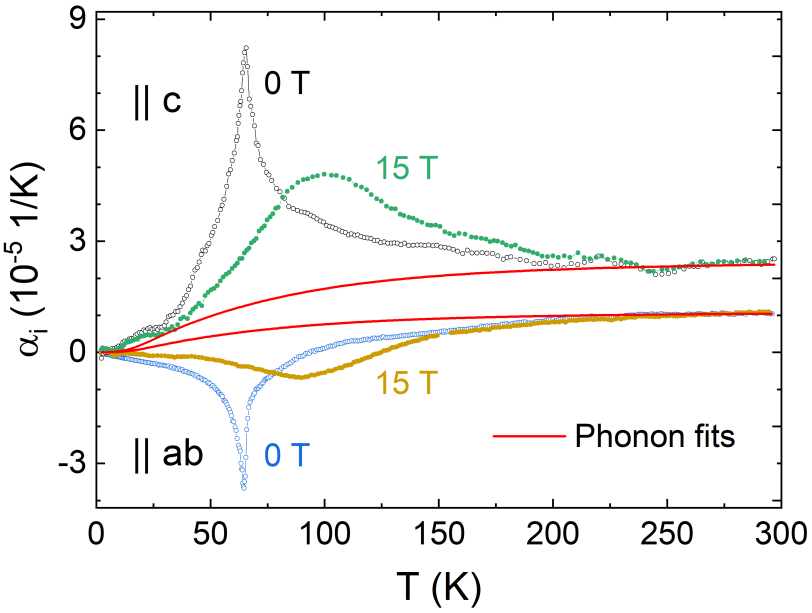

Figure S3. Thermal expansion coefficients α_i of $Cr_2Ge_2Te_6$ at 0 T and 15 T derived from the data in Fig. 1, measured in the standard dilatometer. [4]

IV. EFFECTIVE MAGNETIC GRÜNEISEN FACTORS

The absolute value of the effective magnetic Grüneisen factors, $\gamma_{i,\mathrm{mag,eff}} = |\alpha_{i,\mathrm{mag}}|/c_{p,\mathrm{mag}} = \kappa\gamma_{i,\mathrm{mag}}/(3V_m)$ up to 130 K is shown in Fig. S4. Above 130 K the absolute values of $\alpha_{i,\mathrm{mag}}$ and $c_{p,\mathrm{mag}}$ become small which leads to large error bars and fluctuations in the data, which is why they are not shown. Along the c axis (red closed circles) a nearly constant value is assumed between 40 K and 130 K except between 64 K and 76 K, i.e., at and just above T_C. In this latter temperature regime a sharp peak can be seen with a jump on the low temperature side and a tail on the high temperature side. Below 40 K $\gamma_{c,\mathrm{mag,eff}}$ rises strongly.

$\gamma_{ab,\mathrm{mag,eff}}$ (black closed circles) exhibits a nearly constant value only between 90 K and 125 K, below which it has a rising "background". Here also a rise can be seen in $|\gamma_{ab,\mathrm{mag,eff}}|$ around T_C, but of opposite behavior. The tail is on the low temperature side (roughly 53 K to 65.3 K) whereas the jump can be seen on the high temperature side, between 65.3 K and 67 K.

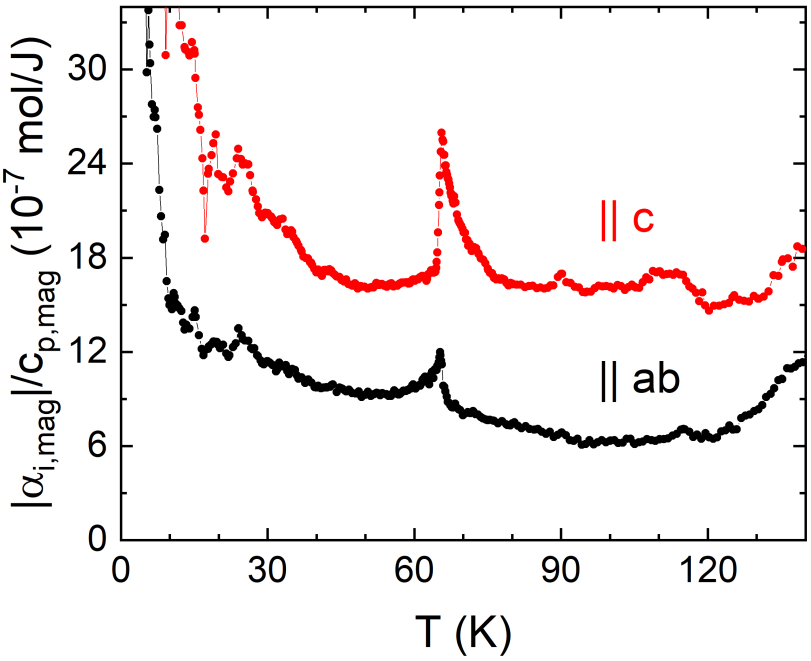

Figure S4. Absolute value of the effective magnetic Grüneisen ratios $\alpha_{i,\mathrm{mag}}/c_{p,\mathrm{mag}}$.

V. HIGH TEMPERATURE MAGNETOSTRICTION

Magnetostriction measurements above $T_C = 65$ K up to 204 K for both $B \parallel ab$ and $B \parallel c$ are shown in Fig. S5. It can be seen that (1) magnetostriction is of opposite sign within the ab plane and along the c axis, (2) magnetostriction along the c axis is about 1.5 times larger than within the ab plane, and (3) at around 150 K (125 K for $B \parallel c$) a sizeable magnetostriction is still present which nearly vanishes around 200 K. The relative length changes from 0 T to 15 T from these measurements as well as measurements below T_C are shown in Fig. 1 in the main text.

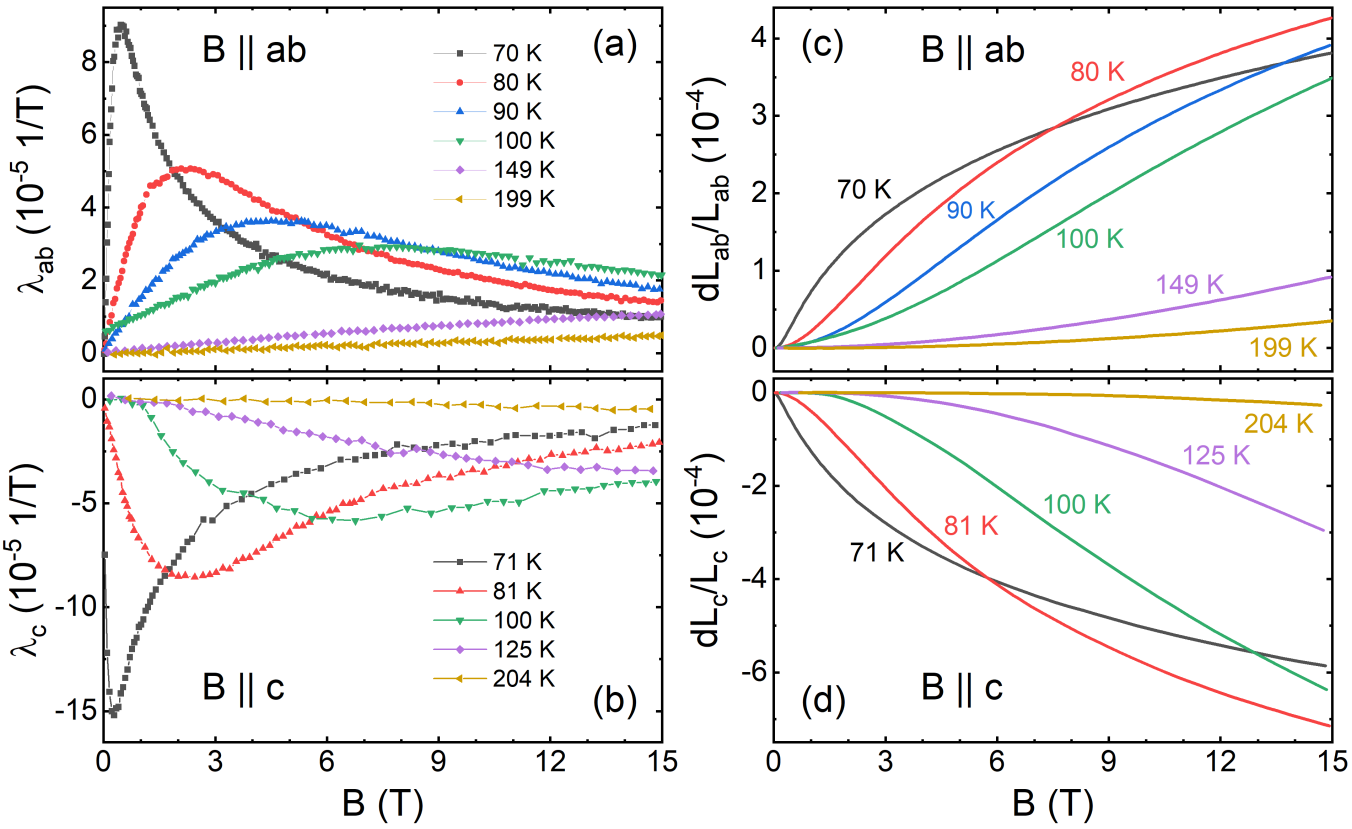

Figure S5. (a, b) Magnetostriction coefficients and (c, d) magnetostrictive relative length changes for $B \parallel ab$ (a, c) and $B \parallel c$ (b, d) at temperatures $T > T_C$. Only up-sweep data is shown.

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