

# Dilatometric studies on single crystalline barlowite – a structurally perfect spin-1/2 kagome system

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## Abstract

We present results of high-resolution thermal expansion measurements on single crystalline barlowite – a structurally perfect spin-1/2 kagome system. The data reveal strongly pronounced and anisotropic second-order phase transition anomalies at the Néel transition at  $T_N = 16$  K. From these data, together with literature results on the specific heat, the uniaxial-pressure dependences of  $T_N$  are derived. We find a rather large positive pressure coefficient for uniaxial pressure along the hexagonal  $c$  axis of  $\partial T_N/\partial p_c = (2.3 \pm 0.2)$  K/GPa and smaller negative in-plane pressure coefficient of  $\partial T_N/\partial p_{\text{in-plane}} = -(0.6 \pm 0.03)$  K/GPa. These effects result in a small positive pressure coefficient under hydrostatic-pressure conditions of  $\partial T_N/\partial p_{\text{hydr}} = (1.1 \pm 0.2)$  K/GPa. Bond-lengths considerations indicate that inter-layer Cu-O bonds, being larger than those typically found in stable Cu-O complexes, are responsible for this behavior.

*Keywords:* Kagome systems, magnetic frustration, thermodynamic properties

## 1 Introduction

The suppression of classical long-range antiferromagnetic magnetic order by geometric frustration has been considered as a promising route in the search for a quantum spin liquid – an entangled macroscopic quantum state for which theory predicts exotic properties [1-3]. Kagome lattices, i.e., corner-sharing triangular lattices, where spin  $S = 1/2$  centers interact through nearest-neighbor antiferromagnetic couplings, are of particular interest for the realization of such a state, due to the combined effects of a high degree of frustration and strong quantum fluctuations, see, e.g. [4,5]. Up to now, however, no perfect  $S = 1/2$  kagome antiferromagnetic system has been synthesized, and accordingly, many theoretical predictions for such a system remain untested. Often small perturbations such as disturbances of the kagome lattice or small anisotropies in the interactions induced, e.g., by the

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Dzyaloshinskii-Moriya (DM) interaction, relieves the system's entropy and long-range order develops at low temperatures.

A class of materials which has been intensively studied with respect to potential spin liquid properties is provided by the Zn-paratacamite family,  $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$  with  $0 \leq x \leq 1$ , forming  $S = \frac{1}{2}$  kagome antiferromagnets [6,7]. The monoclinic clinoatacamite, the  $x = 0$  end member of this series, exhibits distorted kagome layers which are coupled by interlayer magnetic  $\text{Cu}^{2+}$  ions. In this system two successive transitions to long-range ordered phases were observed at 18 K and around 6 K [8], the latter one is accompanied with the occurrence of a ferromagnetic component. For a Zn concentration  $0.33 < x < 1$  the distortion of the kagome lattice is released, leading to a rhombohedral structure with a perfect kagome lattice in the  $a$ - $b$  plane, which still exhibits long-range order around 6 K. A crucial point in these compounds relates to the chemical similarity between  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  which leads to site mixing of Zn and Cu of a few percent in the kagome planes [9]. It is still under discussion how this site mixing influences the ground state properties of the material. An attempt to reduce this problem has been to exchange Zn by Mg [10]. Due to its ligand-field chemistry Mg strongly disfavors the position within the tetragonally distorted  $\text{O}_4\text{Cl}_2$  coordination site in the kagome plane and, by this, ensures minimal substitution of Cu by Mg. It results in a new series of compounds,  $\text{Mg}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$  with  $0 \leq x \leq 0.75$ , that is isostructural with paratacamite and also exhibits magnetic order around 6 K. A substitution of Cu by Zn or Mg with  $0.33 < x$  has, within the experimental resolution, no influence on the lattice constant, the kagome layers and the local Cu environment. There is also no clear influence of  $x$  on the magnetic transition temperature as  $T_N$  stays around 6 K for the various systems.

Of particular interest in this series is the  $x = 1$  end member compound,  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ , called herbertsmithite. This system lacks long-range order down to 50 mK [11] and has been considered a leading candidate for a quantum spin liquid. It features a perfect 2D kagome lattice of  $\text{Cu}^{2+}$  ions in Jahn-Teller-distorted  $\text{O}_4\text{Cl}_2$  octahedra, separated by  $\text{Zn}^{2+}$  embedded in a trigonal oxygen environment. Yet, this system is not free from the Zn-Cu inter-site mixing issue as mentioned above. Interestingly, it has been shown that, by the application of pressure in excess of 2.5 GPa, long-range magnetic order is stabilized around 6 K [12].

Recently, a related Cu  $S = \frac{1}{2}$  containing kagome system has been discussed with respect to its frustrated magnetism [13,14]. It is the natural mineral barlowite,  $\text{Cu}_4(\text{OH})_6\text{FBr}$ , which features a geometrically perfect kagome motif similar to herbertsmithite. Barlowite crystallizes in a hexagonal structure in the  $P6_3/mmc$  space group with lattice parameters  $a = 6.6786(2)$  Å and  $c = 9.2744(3)$  Å [13]. In contrast to herbertsmithite, however, the kagome layers in barlowite are perfectly aligned. This is due to different bonding environments in barlowite adopted by  $\text{F}^-$  (forming hydrogen bonds with six hydroxyl ions) and  $\text{Br}^-$  (forming six covalent bonds to three  $\text{Cu}^{2+}$  ions below and three above) compared to  $\text{Cl}^-$  (which forms both covalent as well as hydrogen bonds) [14]. As a result, barlowite features a higher flexibility with regard to substitutions due to the combination of covalent and hydrogen bonds connecting the kagome layers. Barlowite exhibits canted long-range antiferromagnetic order below  $T_N = 15$  K [13] which has been attributed to the 3D network of exchange couplings together with a substantial Dzyaloshinskii-Moriya interaction [14].

Here we present results of the coefficient of thermal expansion with special focus lying on the low-temperature regime  $T \leq 60$  K, where besides the transition at  $T_N$  indications for multiple phase transitions have been reported [13]. Besides a characterization of the magnetic transition at  $T_N$ , and the search for other phase transitions, these measurements allow for a determination of the uniaxial-pressure coefficients of  $T_N$ . Such information is of importance for a better understanding of the formation of long-range order in these systems and may eventually guide the synthesis of materials where the order can be fully suppressed.

## 2 Experimental

Single crystals of barlowite,  $\text{Cu}_4(\text{OH})_6\text{FBr}$ , of size about  $0.8 \times 0.8 \times 1 \text{ mm}^3$  were grown synthetically as described in ref. [14]. The magnetic properties were measured using a Quantum Design SQUID magnetometer in the temperature range  $2 \text{ K} \leq T \leq 300 \text{ K}$  on a single crystal of mass  $m = 2.4 \text{ mg}$ . The data have been corrected for the temperature-independent diamagnetic core contribution of the constituents [15] and the magnetic contribution of the sample holder. For the thermal expansion measurements, a high-resolution capacitive dilatometer (built after ref. [16]) was used, enabling the detection of length changes  $\Delta l \geq 10^{-2} \text{ \AA}$ . The linear coefficient of thermal expansion  $\alpha(T) = l^{-1}dl/dT$  is approximated by the differential quotient  $\alpha(T) \approx [\Delta l(T_2) - \Delta l(T_1)]/[l(300 \text{ K}) \cdot (T_2 - T_1)]$  with  $\Delta l(T) = l(T) - l(300 \text{ K})$  and  $T = (T_1 + T_2)/2$ . Data were taken along the hexagonal  $c$  axis and along an axis perpendicular to the  $c$  axis, i.e., within the hexagonal plane. The experiments were carried out on a single crystal from the same batch as the crystal studied in ref. [14].

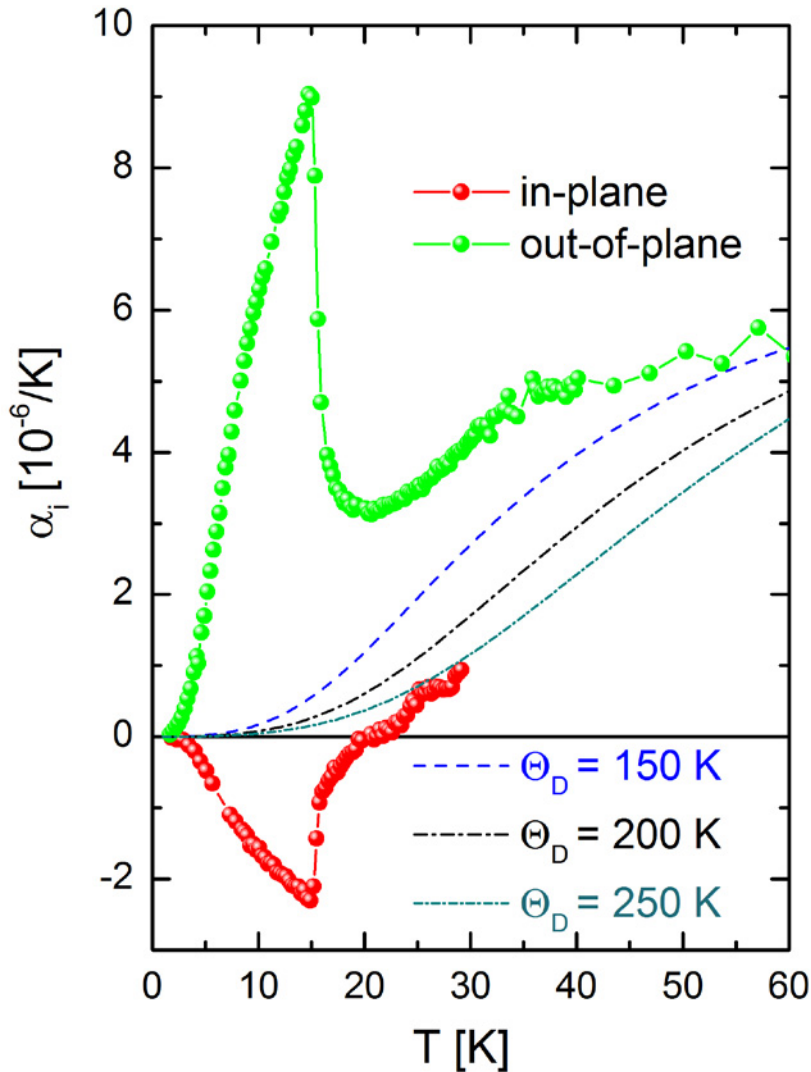
## 3 Results and Discussion

In figure 1 we show the coefficient of thermal expansion measured along and perpendicular to the hexagonal  $c$  axis of a single crystalline barlowite for temperatures  $1.5 \text{ K} \leq T \leq 60 \text{ K}$ . The data reveal a pronounced and strongly anisotropic phase transition anomaly at the magnetic phase transition around 16 K and an anisotropic behavior above.

Starting with the paramagnetic regime  $T \geq 16 \text{ K}$ , we find a slow increase in the out-of-plane expansivity  $\alpha_c$  with increasing temperature superimposed by some weak shoulder around 35 K. The in-plane expansion coefficient  $\alpha_{\text{in-plane}}$  in the paramagnetic range is distinctly smaller and even becomes negative below about 20 K. The figure also shows Debye functions for three different Debye temperatures  $\theta_D = 150, 200$  and  $250 \text{ K}$  which we consider to cover the range for any reasonable Debye temperature of this material. The prefactor was chosen such that the Debye functions roughly match the expected asymptotic behavior of  $\alpha_c$  towards higher temperatures. A more accurate determination of the lattice contribution is, unfortunately, hampered by the lack of a non-magnetic reference material. A comparison of the  $\alpha_c$  data with these Debye functions suggests the presence of a significant magnetic contribution  $\alpha_c^{\text{mag}}(T) > 0$  in the paramagnetic state. Such contributions have been observed in the thermal expansion coefficients of various low-dimensional spin systems in their correlated paramagnetic regime, see, e.g., ref. [17]. A magnetic contribution, albeit with negative sign  $\alpha_{\text{in-plane}}^{\text{mag}}(T) < 0$ , is likely to contribute to the in-plane expansion as well and may provide a natural explanation for the sign change in  $\alpha_{\text{in-plane}}(T)$  below 20 K.

Around 16 K the  $\alpha_i$  data in figure 1 reflect the lattice response at the magnetic transition, which manifests itself in a pronounced anomaly in the magnetic susceptibility,  $\chi$ , plotted as  $d(\chi \cdot T)/dT$  in figure 2b. The anomalies in both the magnetic susceptibility as well as the thermal expansion have the characteristics of a mean-field-type second-order phase transition. From an equal-areas construction in a representation  $\alpha/T$  vs.  $T$  in figure 2a, where the slightly broadened phase transition anomalies can be replaced by ideally sharp ones, we derive a transition temperature  $T_N = 16 \text{ K}$ , consistent with published results [13,14]. In this representation the hump revealed in the  $\alpha_i$  data in figure 1 on the low-temperature side of the transition gives rise to a rather sharp break in the slope around 9 K. However, the absence of

any clear feature in  $d(\chi \cdot T)/dT$  at this temperature (cf. Fig. 2b) speaks against a phase transition as the origin of this anomaly. Likewise, no indications for anomalous behavior is revealed both in the  $\alpha_i$  (Figs. 1 and 2a) and the  $d(\chi \cdot T)/dT$  data (Fig. 2b) around 13.8 K and 26 K where in ref. [13] further phase transitions have been claimed.

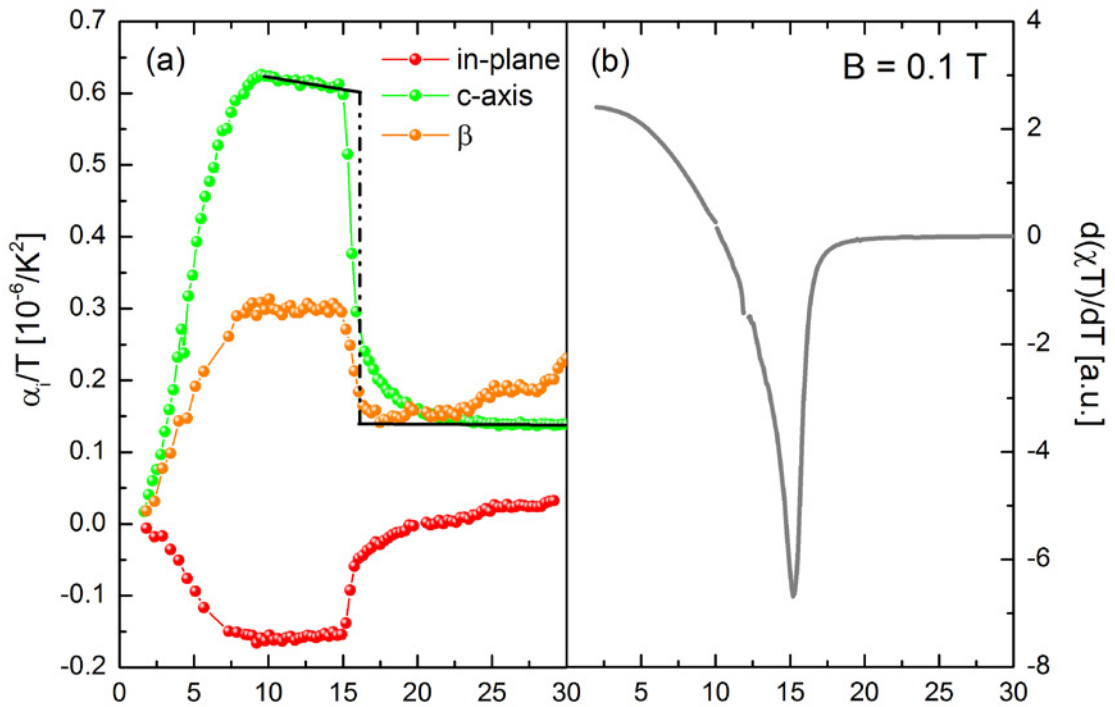


**Figure 1:** Uniaxial coefficient of thermal expansion measured along (green spheres) and perpendicular (red spheres) to the hexagonal  $c$  axis of single crystalline barlowite. Lines represent Debye functions for three different Debye temperatures  $\theta_D$ , as indicated in the figure. The amplitude of the Debye functions have been scaled by a factor such that the model curves roughly match the asymptotic high-temperature behavior of  $\alpha_c$ .

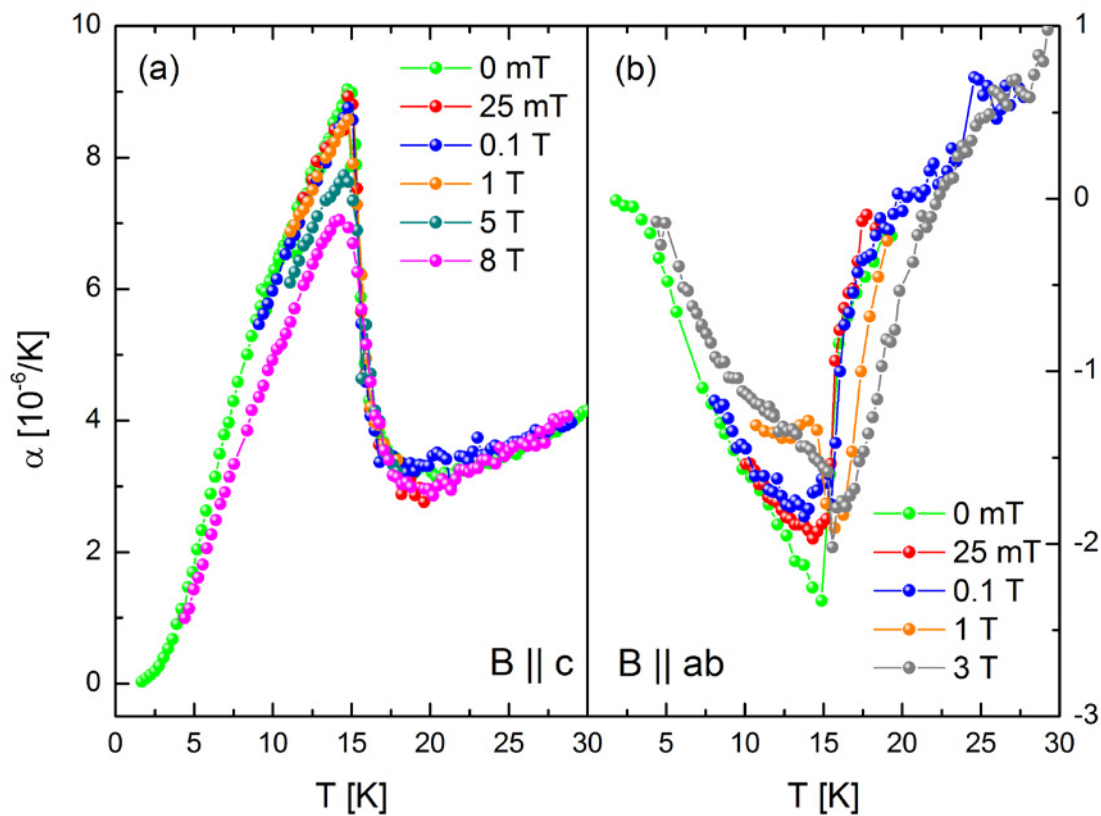
The representation  $\alpha/T$  vs.  $T$  in figure 2a also allows for a precise determination of the discontinuities at  $T_N$ , defined as  $\Delta\alpha_i = \lim_{T \rightarrow T_N} (\alpha_{T < T_N} - \alpha_{T > T_N})$  where  $i = c$  or *in-plane*. We find  $\Delta\alpha_c = (7.4 \pm 0.5) \cdot 10^{-6} \text{ K}^{-1}$  and  $\Delta\alpha_{\text{in-plane}} = - (2.0 \pm 0.1) \cdot 10^{-6} \text{ K}^{-1}$ . According to the Ehrenfest relation, the initial slope of the uniaxial-pressure dependence of  $T_N$  is given by

$$\left( \frac{\partial T_N}{\partial p_i} \right)_{p_i \rightarrow 0} = T_N V_{\text{mol}} \frac{\Delta\alpha_i}{\Delta C_p},$$

where  $\Delta C_p$  is the discontinuity in the specific heat. By using literature results  $\Delta C_p = 5.5 \text{ JK}^{-1}\text{mol}^{-1}$  [13] and  $V_{\text{mol}} = 107.8 \cdot 10^{-6} \text{ m}^3\text{mol}^{-1}$ , we find  $\partial T_N / \partial p_c = (2.3 \pm 0.2) \text{ K/GPa}$  and  $\partial T_N / \partial p_{\text{in-plane}} = -(0.6 \pm 0.03) \text{ K/GPa}$ , i.e., a relatively large, positive pressure coefficient for uniaxial pressure along the hexagonal  $c$  axis and a comparatively small, negative in-plane pressure coefficient.



**Figure 2:** (a) Uniaxial expansion coefficients  $\alpha_i$ , in a representation  $\alpha_i/T$  vs.  $T$ , together with the volume expansion coefficient  $\alpha_v = \beta = 2 \cdot \alpha_{\text{in-plane}} + \alpha_c$ . For the  $\alpha_c$  data we show exemplarily the equal-areas construction used to determine the transition temperature  $T_N$  and the idealized discontinuity in  $\alpha$  and  $\beta$  at  $T_N$ . (b) Magnetic susceptibility measured on the same single crystal as used for the expansivity measurements in a magnetic field  $B = 0.1 \text{ T}$  aligned along the hexagonal plane in a representation  $d(\chi(T)/dT)$  vs.  $T$ .



**Figure 3:** Uniaxial coefficient of thermal expansion along (a) and perpendicular (b) to the hexagonal  $c$  axis of single crystalline barlowite in varying magnetic fields. The magnetic field in the measurements of  $\alpha_c$  (a) was aligned parallel to the  $c$  axis; in the measurements for  $\alpha_{in-plane}$  (b) parallel to the  $a$ - $b$  plane.

As a result of these counteracting effects in  $\alpha_i$ , an only small anomaly is seen in the volume expansion coefficient  $\alpha_v$ , determined by  $\alpha_v = \beta = \alpha_{\perp} + 2 \cdot \alpha_{in-plane}$  for the present hexagonal structure. For the hydrostatic pressure dependence of  $T_N$ , given by  $\partial T_N / \partial p_{hydr} = 2 \cdot \partial T_N / \partial p_{in-plane} + \partial T_N / \partial p_c$ , we find  $\partial T_N / \partial p_{hydr} = (1.1 \pm 0.2)$  K/GPa. The results of the uniaxial pressure dependences indicate that the moderate increase of  $T_N$  under hydrostatic pressure is dominated by the uniaxial pressure component along the  $c$  axis.

It is interesting to compare these observations with results recently obtained by Kozlenko *et al.* [12] in their combined structural and magnetic studies on herbertsmithite at varying pressure. The authors found a pressure-induced phase transition at  $P = 2.5$  GPa from a low- $P$  quantum-disordered spin liquid phase to a long-range ordered antiferromagnetic phase with  $T_N = 6$  K. Such a pressure-induced magnetic order is consistent with recent theoretical calculations for the kagome antiferromagnet, predicting a quantum phase transition from a spin liquid to a spin-frozen state induced by the Dzyaloshinskii-Moriya interaction  $D$  [18,19]. Since in kagome lattices the magnetic bonds lack inversion symmetry, a finite

DM interaction is, in fact, inherent to these systems. With further increasing pressure, the experiments in ref. [12] show that  $T_N$  becomes reduced in a near linear fashion at a rate of about  $\partial T_N/\partial p \approx 0.15$  K/GPa. Moreover, the observed decrease of  $T_N$  upon further compression was found to correlate with anomalies in the pressure response of the Cu-O bond length and the Cu-O-Cu bond angles at ambient temperature, i.e., anomalous structural effects with dominant in-plane components.

From these findings we may conclude that herbertsmithite, in its  $P$ -induced magnetically ordered phase, and barlowite share a suppression of  $T_N$  with increasing in-plane pressure. Given the different response of  $T_N$  under hydrostatic pressure for both systems, viz.  $\partial T_N/\partial p_{\text{hydr}} > 0$  for barlowite and  $< 0$  for herbertsmithite, one can infer that this difference roots in different effects the out-of-plane component of the pressure has for both systems. In searching for structural elements which could be responsible for this different behavior, we mention an observation made in ref. [12] for herbertsmithite. According to that work, hydrostatic pressure only influences the Cu-O octahedra of the kagome planes. At the same time the inter-plane Zn cations in their  $D_{3d}$  crystal field environment, connecting adjacent kagome planes, were found to remain unchanged upon applying pressure [12]. In contrast, in barlowite inter-plane Cu-O bonds exist, connecting Cu-O octahedra of adjacent kagome planes, which are likely susceptible to pressure as their bond lengths are distinctly larger than the ones typically found in stable Cu-O complexes [20]. This may indicate a less stable configuration which can be easily influenced by applying pressure. This not only will change the Cu-O bond lengths but also the Cu-O bond angles and, as a result of both, the exchange coupling constants and  $T_N$ . As for the Cu-O bond lengths inside the kagome plane, the ones found in barlowite are similar to those of herbertsmithite at 2.5 kbar.

In figure 3 we show the results of the uniaxial expansion coefficients measured along (Fig. 3a) and perpendicular (Fig. 3b) to the hexagonal axis under varying magnetic fields applied along the measuring direction. Figure 3a demonstrates that a field applied along the  $c$  axis has only a little effect on the magnetic transition: the size of the discontinuity in  $\alpha_c$  becomes somewhat reduced with increasing field whereas the transition remains sharp with a transition temperature almost unaffected for fields up to 8 T, the maximum field applied in this experiment. This is different for fields applied parallel to the hexagonal plane, cf. Fig. 3b. Here we observe significant rounding effects even for the smallest field applied of 25 mT. With increasing field the high-temperature flank of the transition progressively broadens and shifts to higher temperature. A similar behavior for fields aligned along the hexagonal planes was seen in the specific heat [13]. Compared to the specific heat data, however, the  $\alpha_{\text{in-plane}}$  results of Fig. 3b provide some fine structure: in finite fields a minimum develops in  $\alpha_{\text{in-plane}}$  at a temperature slightly above  $T_N$  in zero field. The rather strong effects observed in  $\alpha_{\text{in-plane}}$  for magnetic fields aligned within the hexagonal plane is consistent with an easy-plane anisotropy of barlowite suggested in ref. [14] based on the analysis of magnetization data. In that work it was argued that the easy plane is a result of the DM interaction.

In summary, in measurements of the uniaxial coefficients of thermal expansion we observe strongly pronounced and anisotropic effects at the Néel transition  $T_N = 16$  K. A large and positive discontinuity is found at  $T_N$  along the out-of-plane hexagonal  $c$  axis, corresponding to a positive pressure coefficient of  $T_N$  for uniaxial  $c$ -axis pressure. In contrast, a distinctly smaller and negative discontinuity occurs along the in-plane axis, corresponding to a negative in-plane pressure coefficient. As a result of the dominating  $c$ -axis effect, a small but positive effect of pressure on  $T_N$  under hydrostatic pressure is expected. Considerations of bond lengths indicate that inter-layer Cu-O bonds are responsible for this behavior.

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