The Origin of Magnetic Ordering in a Structurally-Perfect Quantum Kagome Antiferromagnet

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The ground state of the simple Heisenberg nearest-neighbor quantum kagome antiferromagnetic model is a magnetically disordered spin liquid, yet various perturbations may lead to fundamentally different states. Here we disclose the origin of magnetic ordering in the structurally-perfect kagome material YCu$_3$(OH)$_6$Cl$_3$, which is free of the widespread impurity problem. 

Quantum spin liquids are magnetically disordered, yet highly entangled states, promoted by quantum fluctuations on some geometrically frustrated spin lattices [1]. A paradigm predicting such a state even at zero temperature is the two-dimensional (2D) nearest-neighbor quantum kagome antiferromagnetic model (KAFM) [2–4], represented by Heisenberg, i.e., isotropic $J_1$ exchange bonds between spins-1/2 sites in Fig. 1. Yet, even small perturbations to this simple model can stabilize fundamentally different ground states, as their influence is strongly amplified by frustration. Various factors, including further-neighbor exchange interactions [5–11], magnetic anisotropy [9–14], defects [14–16], and structural distortions [17] have been the focus of theoretical investigations in recent years. One of the seminal predictions that still calls for a clear experimental validation is a quantum critical point induced by Dzyaloshinskii-Moriya (DM) magnetic anisotropy, separating a spin liquid from a magnetically ordered ground state of KAFM [12]. Here we elucidate the role of the DM interaction in promoting correlations that lead to the condensation of magnetic order in a material that closely realizes the KAFM.

Actual KAFM realizations are as a rule plagued by several perturbations, which makes experimental assessment of the individual roles of these perturbations challenging. A direct consequence of many effects being intertwined is that even the existence of a spin gap in the spin-liquid ground state of the KAFM remains unsettled. In fact, for the hitherto most intensively studied KAFM material herbertsmithite [19], indications of a finite gap [20] have been recently superseded by the conclusion that the gap is absent [21]. However, it remains unknown to what extent particular perturbations present in this material affect its low-energy magnetism. Relevant imperfections include sizable inter-site ion mixing [22–24], large DM anisotropy [25] and subtle structural distortion away from perfect kagome symmetry [26, 27]. On the contrary, in the recently synthesized KAFM ma-

![FIG. 1. Weiss temperature $\theta_W$ of YCu$_3$(OH)$_6$Cl$_3$ determined from DFT+$U$ calculations for different values of the effective on-site Hubbard repulsion $U_{\text{eff}}$ (points). The dashed line shows the experimental value $\theta_W = -99$ K, while the solid line serves as a guide to the eye. The inset depicts two neighboring kagome layers of Cu$^{2+}$ spin-1/2 ions with inplane Heisenberg exchange interactions $J_1$ (solid arrows) and interplane inter-

$J_1'$ (dashed arrows). The nearest-neighbor coupling $J_1$ is by far the dominant one [18].]
terial YCu$_3$(OH)$_6$Cl$_3$ [28] all structure-related perturbations, including the inter-site disorder, are absent [28, 29]. Therefore, the recent discoveries of static internal magnetic fields [29, 30] and magnetic Bragg peaks [31] that develop in this material at low temperatures are rather surprising. Experiments have further established that the average ordered Cu$^{2+}$ magnetic moment of an otherwise regular 120° magnetic structure is strongly reduced [31] and is accompanied by spin fluctuations persisting down to the lowest accessible temperatures [30]. The origin of such exotic magnetism is unknown, but even more fundamentally, the basic question of the magnetic-ordering mechanism present in this material remains unexplained. Since YCu$_3$(OH)$_6$Cl$_3$ is a unique KAFM material with a limited number of possible perturbations, determining the ordering mechanism would be very important for assessing the impact of these perturbations on the spin-liquid ground state of pure KAFM.

Here we show a combination of density functional theory (DFT), finite-temperature Lanczos method (FTLM) and electron spin resonance (ESR) results, which allows us to address the origin of the unexpected magnetic ordering at nonzero temperatures in YCu$_3$(OH)$_6$Cl$_3$. The DFT calculations together with modeling of the magnetic susceptibility show that the nearest-neighbor Heisenberg exchange $J_1 = 82(2)$ K is by far the dominant isotropic interaction. The ESR measurements together with the FTLM modeling of specific heat, on the other hand, reveal an additional sizable out-of-plane DM anisotropy $D_z/J_1 = 0.25(1)$ that places the investigated compound in the magnetically-ordered region of the KAFM phase diagram [12]. Moreover, the FTLM modeling provides a novel insightful view into the role of the DM interaction in KAFM. This interaction leads to a low-temperature peak in specific heat related to enhancement of the spin correlations within the kagome planes, which allows for precise determination of its magnitude.

To understand the magnetism of YCu$_3$(OH)$_6$Cl$_3$, the first task is to determine its dominant isotropic exchange interactions. As in other kagome compounds [32–35], we tackle this problem using total-energy (broken-symmetry) DFT+$U$ calculations [36] (for details see Ref. 18). We assume that each site is coupled with sites up to the third nearest neighbor in the kagome layer and with equivalent sites in the neighboring two kagome layers (Fig. 1). Our calculated exchange constants and the corresponding Weiss temperature $\theta_W = -\sum z_i J_i / 4$, where $z_i$ is the number of neighbors coupled to a particular site with $J_i$ [37], depend on the effective on-site Hubbard repulsion $U_{\text{eff}}$ [18]. $\theta_W$ is compared with its experimental value of $-99(1)$ K, which is obtained from a Curie-Weiss fit to susceptibility data (inset in Fig. 2). The experiment is well reproduced for $U_{\text{eff}} = 6$ eV (Fig. 1), a value consistent with previous studies on similar materials [32–35]. We find that the exchange interaction between nearest neighbors $J_1 = 84.2(4)$ K by far exceeds all other Heisenberg interactions, as all of them are below 5% of $J_1$, regardless of the exact value of $U_{\text{eff}}$ [18].

Next, we focus on the temperature dependence of the magnetic susceptibility to verify that the calculated exchange constants are consistent with experiment. We first compare the experimental susceptibility [30] to a high temperature series expansion (HTSE) prediction for a simplified $J_1$-$J_2$-$J_3$ model [38] in Fig. 2. The HTSE curve fitted in the temperature range between 100 and 300 K matches the experiment very well and yields the exchange constants $J_1 = 79.5(1)$ K, $J_2 = 2.8(27)$ K, and $J_3 = 4.3(54)$ K. Furthermore, we can compare the experiment to FTLM calculations for a pure nearest-neighbor KAFM on a $N = 42$ spin cluster [39]. A good agreement is obtained for temperatures down to 0.6 $T_J / K$ with $J_1 = 82.2(1)$ K being the only free parameter (Fig. 2).

The fact that all three independent approaches yield very similar predictions, namely a dominant Heisenberg exchange interaction $J_1 = 82(2)$ K, gives strong credibility to these results. As isotropic exchange interactions beyond the nearest neighbors are limited to at most 5% of $J_1$, YCu$_3$(OH)$_6$Cl$_3$ can be placed alongside herbertsmithite [33] as one of the best realizations of the nearest-neighbor KAFM. In all other well studied examples, like kapellasite [32, 34, 38], haydeeite [32, 34, 41], volborthite [42], and vesignieite [43], further-neighbors interactions...
are much larger. As interactions $|J_2|$, $|J_3|$, $|J_d| \gtrsim 0.2 J_1$ [5–7, 9] or $|J'| \gtrsim 0.15 J_1$ [8] are needed to induce magnetic ordering in KAFM, these are evidently too small in YCu$_3$(OH)$_6$Cl$_3$. The only remaining perturbation that can account for its ordered ground state is magnetic anisotropy between nearest neighbors. Since there are no symmetry restrictions [44], this could either take the form of the antisymmetric DM interaction $D \cdot (S_i \times S_j)$, or the symmetric easy-plane anisotropic exchange (AE) interaction $\Delta (2S^z_i S^z_j / 3 - S^x_i S^x_j / 3 - S^y_i S^y_j / 3)$.

The next task is, therefore, to determine the dominant magnetic anisotropy term in YCu$_3$(OH)$_6$Cl$_3$. First, we note that further-neighbor isotropic exchange interactions are too small to explain the large discrepancy between the experimental magnetic susceptibility and the FTLM prediction already at temperatures as high as $0.6 J_1 \sim 50 K$ (Fig. 2), therefore, magnetic anisotropy should be larger than these interactions. We can quantify the anisotropy using ESR (for details see Ref. 18), as anisotropy directly broadens the ESR spectra [45]. The measured spectra (inset in Fig. 3) are broader than in other Cu-based kagome compounds like herbertsmithite [25], vesignieite [46], and kapellasite [47] by almost an order of magnitude. Above $200 K$ the ESR line width is constant at $\Delta B = 6.8(5) T$ (Fig. 3), which is consistent with a high-temperature paramagnetic regime and allows for the application of the well-established Kubo-Tomita theory [48]. For the powder-averaged full width at half maximum (FWHM) we get [25, 46]

$$\Delta B = \frac{k_B}{g \mu_B} \frac{\alpha A^2}{J_1},$$

where $k_B$ is the Boltzmann constant, $\mu_B$ the Bohr magneton and we consider only the dominant nearest-neighbor isotropic interaction. The constant $\alpha$ is $3/4$ for the out-of-plane DM interaction $A = D_z$, $5/(4 \sqrt{3})$ for the in-plane DM interaction $A = D_p$, and $3/(2 \sqrt{3})$ for the AE interaction $A = \Delta$. Taking $g = 2.077$ and $J_1 = 82 K$, we obtain separately the estimates $D_z = 24(2) K = 0.29(3) J_1$, $D_p = 35(3) K = 0.43(4) J_1$, and $\Delta = 27(3) K = 0.33(3) J_1$. We note that the DM anisotropy is generally dominant in Cu$^{2+}$-based magnets, because it is a lower order correction to the isotropic exchange than the AE interaction [44], so that the ratio $\Delta/D \sim \Delta g/g \sim 0.15$ is expected for the Cu$^{2+}$ ions [49]. Furthermore, as the easy-plane AE interaction is not expected to lead to magnetic order of KAFM [13, 50], we attribute the large experimental ESR line width to the DM interaction.

The dominant DM component is determined from the temperature dependence of the magnetic susceptibility (Fig. 2). According to exact-diagonalization (ED) calculations for the kagome lattice [40], the out-of-plane component $D_z$ suppresses the susceptibility when compared to the isotropic model, while the in-plane component $D_p$ enhances it. The experimental suppression of the susceptibility implies $D_z$ is of the order $D_z/J_1 = 0.2–0.3$. Since this agrees well with our estimate $D_z = 0.29(3) J_1$ based on the ESR line width, this is obviously the dominant DM component in YCu$_3$(OH)$_6$Cl$_3$.

An independent check of the above-estimated DM anisotropy is provided by modeling our previously published zero-field specific heat ($c$) data [30]. FTLM calculations [51, 52] of the magnetic contribution to the specific heat $c_m$, which were performed on spin clusters with up to $N = 30$ spins for various ratios $D_z/J_1$ (for details see Ref. 18), reveal two well-resolved peaks in $c_m$ for $D_z/J_1 \gtrsim 0.08$ (Fig. 4a). A broad high-temperature peak around $0.67 J_1$ does not shift with $D_z/J_1$, while a narrower low-temperature peak shifts almost linearly with $D_z$ and is found at $T_{\text{max}} \simeq 0.91 D$ (inset in Fig. 4a). The high-temperature peak is at a similar position as for a spin-1/2 square lattice [53] and reflects enhancement of nearest-neighbor spin correlations [54, 55]. On the other hand, we find that the low-temperature peak, with its linear dependence on $D_z$, corresponds to growing 120$^0$ spin correlations on basic triangular units of the kagome lattice, as the out-of-plane DM component linearly shifts the energy of such a chiral spin structure [31].

For $D_z/J_1 = 0.25$, the low-temperature peak exactly coincides with the broad anomaly in the experimental $c/T$ curve (inset in Fig. 4c). Indeed, we can fit the experimental data very well with the sum $c = c_m + c_{\text{ph}}$, which includes a Debye phonon contribution $c_{\text{ph}}$ with a Debye temperature $\theta_D = 224(5) K$. The obtained value $D_z/J_1 = 0.25(1)$ is in good agreement with the estimate $D_z/J_1 = 0.29(3)$ based on the ESR line-width analysis, especially when considered that the Kubo-Tomita theory might be overestimating $D_z$ on the kagome lattice, as concluded from ED calculations of the ESR line width on finite spin clusters [56]. The value $D_z/J_1 = 0.25(1)$

![FIG. 3. The ESR FWHM with the horizontal line highlighting its temperature independence above 200 K. The inset shows a selected ESR spectrum of YCu$_3$(OH)$_6$Cl$_3$ (circles) with the corresponding Lorentzian fit (line).](image-url)
also convincingly explains the suppression of the magnetic susceptibility shown in Fig. 2. Although the DM anisotropy in YCu$_3$(OH)$_6$Cl$_3$ is larger than in some other Cu$^{2+}$-based KAFM materials [25, 46], its size is still compatible with the order-of-magnitude estimate [44] $D_2/J_1 \sim \Delta g/g \sim 0.15$ for the Cu$^{2+}$ ions [49]. We note that the comparison of the FTLM curves and the experimental magnetic contribution to the specific heat shown in Fig. 4c demonstrates that $c_m$ is a very sensitive probe of the DM interaction on the kagome lattice.

Having established the size of the main terms in the spin Hamiltonian of YCu$_3$(OH)$_6$Cl$_3$, we are now in position to discuss the origin of its magnetic ordering. It is theoretically well established that the out-of-plane DM interaction leads to a $q = 0$ long-range order of KAFM at zero temperature if its strength exceeds the critical value $D_2 = 0.10(2)J_1$ [9, 10, 12, 14] separating the spin-liquid and the ordered phase. Contrary to the paradigmatic KAFM material herbertsmithite, which appears to be on the verge of criticality [25], we find that YCu$_3$(OH)$_6$Cl$_3$ is well inside the ordered phase. Nevertheless, the average ordered moment should be strongly suppressed due to quantum fluctuations. Indeed, the predicted moment of $0.35 \mu_B$ for $D_2/J_1 = 0.25$ [12] matches reasonably well with the experimental value of $0.42(2) \mu_B$ [31].

We can comment on the compatibility of our results with the celebrated Mermin–Wagner theorem [57], which precludes long-range order in the considered 2D model at nonzero temperatures due to continuous in-plane symmetry. The observed 3D order at a finite temperature $T_N$ [30, 31], therefore, requires interlayer interactions. The transition temperature is determined by the growth of the in-plane correlation length $\xi$ (in units of the nearest-neighbor distance) to the extent that the thermal energy will drop below the energy of interaction of short-range ordered 2D regions on neighboring kagome planes, when $T_N \approx (\xi(T_N))^{2}J/S(S + 1)$ [54, 55]. As $\xi$ should only marginally depend on the inter-layer interaction for $J'/J_1 \ll 1$ and thus should $T_N$ only logarithmically depend on $J'$ [53, 55, 58], $T_N$ is dominantly determined by $D_2$ in YCu$_3$(OH)$_6$Cl$_3$. The role of the DM interaction is to promote building up of the $120^\circ$ spin correlations within the kagome layers, which corresponds to effectively shifting a large release of the system’s entropy to temperatures $T \approx D_2$ (Fig. 4b). We note that for $J'/J_1 \ll 1$ the release of the entropy at $T_N < T_{\text{max}}$ becomes very small as most of the entropy is already released around $T_{\text{max}}$ due to substantial 2D spin correlations. Consequently, the expected anomaly in specific heat at $T_N$ becomes unobservable [53], which likely explains its absence in YCu$_3$(OH)$_6$Cl$_3$.

In conclusion, YCu$_3$(OH)$_6$Cl$_3$ turns out to be an extremely rare structurally-perfect KAFM material, with the nearest-neighbor isotropic exchange interaction $J_1 = 82(2)\text{K}$ dominating all other isotropic interactions, while the most relevant perturbation is the out-of-plane DM anisotropy $D_2/J_1 = 0.25(1)$. This ratio places the system in the magnetically-ordered part of the theoretically-predicted phase diagram [12]. This provides an unambiguous experimental confirmation of the key role of the DM interaction in inducing the magnetic order on the kagome lattice. Furthermore, now that the role of the
DM interaction is well understood, a sister compound \( \text{Y}_3 \text{Cu}_6 (\text{OH})_2 \text{OCl}_8 \) with a slightly distorted kagome lattice and apparently a spin-liquid ground state [29] provides an ideal opportunity to study the effects of further perturbations. Since in the latter compound very similar exchange interactions and magnetic anisotropy as in \( \text{YC}_3 \text{(OH)}_2 \text{Cl}_3 \) are expected, the reasoning for its lack of magnetic ordering should be searched in deviations from the perfect kagome symmetry.

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Supplemental Information: The Origin of Magnetic Ordering in a Structurally-Perfect Quantum Kagome Antiferromagnet

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DFT CALCULATIONS

Ab-initio calculations were performed using the CASTEP DFT code [1] using a local (spin) density approximation (LDA) functional with an additional effective on-site Hubbard repulsion $U_{\text{eff}} = U - J_H = 4$–7 eV, where $U$ is the bare Hubbard repulsion and $J_H \approx 1$ eV is Hund’s coupling, which was kept fixed. An LDA+$U$ functional was chosen over a more sophisticated generalized gradient approximation (GGA) functional, as recent results suggest [2] that it can, in certain cases, perform better than standard GGA+$U$ functionals [3] when describing the magnetism of materials.

For each value of $U_{\text{eff}}$ the starting $173(2)$ K experimental crystal structure from Ref. 28 was relaxed with free lattice in internal structural parameters, resulting in unit cells with 93(1)% of the experimental cell volume. Well-converged total DFT energies of 102 random collinear spin configurations in a $2 \times 2 \times 2$ supercell containing 24 Cu$^{2+}$ ions were then calculated and finally fitted in the total-energy (broken-symmetry) DFT framework [5] by a spin model described by 9 Heisenberg exchange interactions depicted in Fig. 1 of the main text plus an energy offset. The results of these fits as well as the derived Weiss temperatures $\theta_W = -\sum_i z_i J_i/4$ are summarized in Table I. We note that even though the true spin ground state of YCu$_3$(OH)$_6$Cl$_3$ is noncollinear [6], the dominant exchange couplings extracted from collinear total-energy DFT calculations are still expected to be reliable, as was also found in other frustrated systems [5, 7–10]. The reason for this is that we are concerned with parametrizing the isotropic part of the system’s spin Hamiltonian, for which knowing the energies of (excited-state) collinear spin configurations is sufficient.

**ELECTRON SPIN RESONANCE**

Electron spin resonance (ESR) measurements were performed at the National High Magnetic Field Laboratory, Tallahassee, USA on a custom-made transmission-type ESR spectrometer with homodyne detection equipped by a sweepable 15-T superconducting magnet. The measurements were performed in the Faraday configuration at the irradiation frequencies of 212.6 and 256.3 GHz on a 770-mg sample from the same batch as used in our previous investigations [6, 12]. A modulation field of about 2 mT was used to record the so-called derivative spectra. The ESR spectra are a mixture of absorption and dispersion, with the corresponding phase determined from fits with the Lorentzian line shape. In order to show pure absorption spectra, the spectra shown in Fig. 5 are phase corrected. The Lorentzian line shape of the ESR spectra is a sign of exchange narrowing due to strong exchange interactions [13]. When fitting the spectra, we fixed the $g$ factor to $g = 2.077$, as deduced from the Curie-Weiss analysis, because the spectra are too broad for a reliable $g$-factor determination. At $T \lesssim 150$ K the fits become unreliable, since the spectra disappear in the noise.

| $U_{\text{eff}}$ (eV) | 4   | 5   | 6   | 7   | HTSE  |
|----------------------|-----|-----|-----|-----|-------|
| $J_1$ (K)            | 107.3(5) | 94.2(4) | 84.2(4) | 85.2(4) | 79.5(1) |
| $J_2$ (K)            | 5.2(5) | 4.1(5) | 3.7(4) | 3.0(4) | 2.8(27) |
| $J_3$ (K)            | 4.2(4) | 3.2(3) | 2.6(3) | 1.8(3) | /      |
| $J_4$ (K)            | 4.5(6) | 3.8(5) | 3.6(4) | 2.6(4) | 4.3(54) |
| $J'_1$ (K)           | 0.9(5) | 0.7(4) | 0.7(4) | 0.1(4) | /      |
| $J'_2$ (K)           | -0.2(3) | 0.1(2) | -0.2(2) | 0.0(2) | /      |
| $J'_3$ (K)           | 2.0(3) | 1.9(3) | 1.9(2) | 1.7(2) | /      |
| $J'_4$ (K)           | 0.3(1) | 0.4(1) | 0.3(1) | 0.3(1) | /      |
| $W$ (K)              | 125.5(7) | 110.5(6) | 98.6(5) | 96.7(14) | /      |

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**Table I.** Isotropic exchange coupling constants of YCu$_3$(OH)$_6$Cl$_3$ calculated by DFT+$U$ for various values of the effective on-site Hubbard repulsion $U_{\text{eff}}$. The last column corresponds to HTSE modeling of magnetic susceptibility (see Fig. 2 in the main text). The considered inplane constants $J_i$ and interplane constants $J_i'$ are defined in Fig. 1 in the main text. The Weiss temperature is $\theta_W = -\sum_i z_i J_i/4$, where $z_i$ denotes the number of neighbors coupled to a particular site by $J_i$. [11].
FIG. 5. The temperature dependence of the ESR spectra of YCu$_3$(OH)$_6$Cl$_3$ measured at 256.3 GHz (circles) with the corresponding Lorentzian fits (solid lines). The spectra are shifted vertically for clarity.

FTLM CALCULATIONS

We consider only the nearest-neighbor exchange spin-$1/2$ Heisenberg model on the kagome lattice, with additional Dzyaloshinskii-Moriya (DM) interaction with only the out-of-plane component $D_z \neq 0$, which applies well to YCu$_3$(OH)$_6$Cl$_3$. The corresponding Hamiltonian is

$$\mathcal{H} = \sum_{\langle ij \rangle} \left[ JS_i \cdot S_j + D_{ij} (S_i \times S_j)_z \right],$$

(2)

where $D_{ij} = \pm D_z$, depending on the direction of the bond [14].

Within this model we calculate entropy per site $s(T)$, and consequently the specific heat $c(T) = T dS / dT$, using the finite-temperature Lanczos method (FTLM) [15, 16], previously used in numerous studies of static (and dynamical) properties at $T > 0$ in various models of correlated electrons [17], including thermodynamic quantities of the pure Heisenberg model on the kagome lattice [18]. Since the $D_z \neq 0$ model still retains the conservation of $S^z_{\text{tot}}$ as well as the translational symmetry (due to periodic boundary conditions), the memory and CPU time requirement for a given system size $N$ are essentially that of the Lanczos procedure for the ground state, provided that we scan over all (different) symmetry sectors $S^z_{\text{tot}}$ and wavevectors $q$, and in addition perform a modest sampling over initial wavefunctions with $N_s = 30$. In the present study we thus deal with the kagome lattices with up to $N = 30$ sites, where the biggest symmetry sector contains $N_{\text{st}} \sim 16 \times 10^6$ basis states.

While FTLM is quite accurate for a given finite-size system, the main concern is the macroscopic ($N \rightarrow \infty$) validity of obtained results [15, 16]. Typically, the criterion $T > T_{\text{fs}}$ is related to the grandcanonical sum $Z(T) = \text{Tr} \{ \exp \{ - (\mathcal{H} - E_0) / T \} \}$, where $E_0$ is the ground-state energy and we require $Z > Z(T_{\text{fs}}) \gg 1$. Since $Z(T)$ is closely related to entropy $s(T)$, this requirement in actual systems effectively reduces to $s > (0.07 - 0.1)k_B$. Fortunately, frustrated systems are characterized by large $s(T)$ at low temperatures and consequently $T_{\text{fs}} \ll J$. This is particularly the case for the pure Heisenberg ($D_z = 0$) model on the kagome lattice (Fig. 4b in the main text; see also the finite-size analysis in Ref. 39). To demonstrate that finite-size effects are small in the considered temperature range where $s(T) > 0.07$, we present in Fig. 6 the comparison of FTLM results for $c(T)$ obtained on lattices with $N = 24, 27$, and 30 sites. The finite-size effects are somewhat enhanced only for the $D_z = 0$ model at $T/J_1 < 0.15$.

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