nature portfolio

Peer Review File

Unique magnetic transition process demonstrating the effectiveness of bond percolation theory in a quantum magnet

Corresponding Author: Professor Xu-Guang Zheng

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript by X.-G. Zheng et al. analyzes a new structural polymorph of atacamite via MuSR, synchrotron-, neutron diffraction, specific heat and SQUID measurements.

Observations:
The synchrotron data clearly suggests a new structural modulation with notably 10 Cu sites, strengthened by the changed magnetic properties.
Such a complex structure is by far no ideal system for physics.
Magnetic susceptibility measurements reveal a Curie Weiß temperature of -170K, a transition is however observed around 7.5 K.
In specific heat, with the given lattice contribution magnetic entropy starts to be released around 10 K, peaks at 5.5K and only reaches 20% of RIn2.
The MuSR spectra are described by four components, where the magnetic order (MO) seems to set in at 20 K, by a loss in asymmetry,
but full static order is only observed at the coinciding specific heat maximum at 5.5 K.
In neutron diffraction two magnetic bragg peaks were observed only at 1K, which were still absent at 9 and 30 K.
Based on two visible magnetic bragg peaks refinement was done were the 6 models are basically indistuingishable.

With a novel system and the given techniques it is suitable for Nature Comm.
After addressing the following points the paper values publication in Nature Communications:
1. The compound is sold as an experimental realization of the bond percolation theory in a quantum magnet based on the good agreement of
0.492(8) as a threshold compared to 2D square lattice calculations with a value around 0.593. Here other values should be compared as this is not an obvious good fit on the first glance.
2. The MuSR analysis notably calls for a reinvestigation of the specific heat,
as the lattice contribution seems to be captured in the temperature range of 10-22 K, while MuSR suggest that there already is magnetic contribution
(atleast I can see no higher T data for specific heat and it is not mentioned in the text).
3. Indeed no magnetic bragg peaks are visible at 9 K, but given the low static ordered fraction, the signal is likely missed in the high noise.
4. The authors claim to have solved the Clinoatacamite mystery.
However it turns out that similar to Clinoatacamite in this trigonal variant around 18 K a first onset of order occurs.
In general the magnetic properties seem not too different than in Clinoatacamite. Given the synthesis technique of the system without water,
a parallel to YCu3(OH)6OxCl3-x is likely (https://doi.org/10.1103/PhysRevMaterials.3.074401).
Where some of the Cl is substituted by O/OH when coming in contact with water.
Notably here the authors have washed their sample afterwards, so possibly a substitutional effect is corrected.
Likely however with only powder and these many positions an occupational refinement is not feasible.

Reviewer #2

(Remarks to the Author)
The authors studied a unique magnetic transition from short-range-ordered spin clusters into a long-range order matching the bond percolation theory in a new quantum antiferromagnet Cu4(OH)6Cl2. There are some issues that the authors need to address clearly. I suggest that they make major revisions carefully before the final decision.

1.The author claim that intermediate magnetic order in clinoatacamite was built in its (101) lattice plane, which then was transformed by the inter-Kagome-layer couplings into a three-dimensional low-temperature spin order. What is the evidence? What is the relationship between this article and the three references cited?
2.The manuscript has some spelling and grammatical mistakes. It should be thoroughly proof-read.
3.How to absolutely confirm the appearance of the short-range order in the studied system? Can STEM or PDF observe more clearly?
4.How to comprehend the pinning effect on the magnetic transition in spin liquids?
5.Can theoretical calculation confirm the possible magnetic structures in Fig.6?

Reviewer #3

(Remarks to the Author)
Authors reported a detailed study on pseudotrigonal Cu4(OH)6Cl2 . This is an interesting study since it presents a unique magnetic system to demonstrate a complete bond percolation process toward the critical transition. The study is interesting for a wide range of readers and the related experimental results are encouraging and well explained. So, it therefore deserves publication. However, I have the following concerns:

(1) The authors should provide the error bars for the values of parameters obtained from their measurements such as lattice parameters then the readers can have a clear idea on the accuracy of values reported. I do not believe that the accuracy for the data listed (5 digital) in Extended Data Table 1 is so high.
(2) In Figure 6, it is clear that two strong reflections (one at around d=5.5Å and around d=10Å) were not fitted well in both models, why? Moreover, the accuracy of magnetic moment looks like not correct (0.08) based on the ration of signal to noise of neutron data

Once this is done, the impact of the work will be visible. So, I recommend 'minor Revision' for this manuscript.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript presents some interesting work worthy of Nature Communications and the authors have addressed all major concerns.

Reviewer #4

(Remarks to the Author)
The authors report magnetic characterisation of a new triclinic polymorph of Cu2(OH)3Cl using μSR and neutron diffraction. The current manuscript lacks in clearly providing the similarity and difference in the crystal/magnetic structure, magnetic connectivity and magnetic properties between the current compound and the heavily studied polymorph, clinoatacamite, and therefore I do not think it is suitable for wide readership of Nature Communications. I also have some technical but serious concerns on the analysis of diffraction data, as below.

Since the triclinic structure has not been reported elsewhere and is central to the discussion, it deserves further scrutiny. The unit cell presented in Extended Data Table 1 is close to rhombohedral symmetry in the sense that a~b~c and alpha~beta~gamma. Which peaks are new, split, or broadened in the triclinic crystal structure compared to the subgroups of R-3m, assuming that the structure derives from that of paratacamite? Le-Bail fits will be helpful to reliably determine the correct space group and subsequent analysis of the crystal structure. Unless deuteration is incomplete, it is also recommended to refine X-ray and neutron diffraction data simultaneously to obtain the hydrogen position and atomic displacement parameters of all the atoms.

Considering the small amount of the sample used for the diffraction experiment, absence of magnetic Bragg peaks at 9 K could be just attributed to a small size of the ordered moment. Although authors states that magnetic peaks are visible in clinoatacamite at 9 K, the cited refs. 22 and 23 are unavailable. Structural refinement against the neutron powder diffraction data readily tells the ordered moment size in μB unit at 1 K, which could be compared to Fig.5d data. In order to claim that the intermediate phase is spin liquid or short-range ordered state, one should at least estimate the largest possible moment

size at 9 K by comparing to the background signal.

Version 2:

Reviewer comments:

Reviewer #4

(Remarks to the Author)
I have listed below potential issues and suggested improvements in the revised manuscript. However, I still wonder if the finding in the triclinic polymorph would have a sufficiently broad impact. Is the short-range ordered phase just above the ordering temperature in frustrated magnets so novel and surprising? Even if some of the properties reported for clinoatacamite turned out to be those of the current compound, what would be the significance of it, since in the end they are in the same class as the distorted pyrochlore structure? These impression might change if the authors were to describe in detail the difference in the crystal structures and show how the difference leads to the contrasting magnetic interactions and magnetic structures and the presence of the intermediate phase, but that would involve a significant change.

1. In Extended Data Fig. 3, what space groups and unit cells are used for the “trigonal” and “primitive” ones, how are they related, and what is the Miller indices of each peak? In the subgroups of R-3m and supergroups of P-1, there are five monoclinic space groups (C2/m, C2/c, P2/c, P21/c, and P21/m), and therefore these should be tested as well. This exercise might find a simpler description of the crystal structure.

2. Addition of magnetic connectivity in Fig.1 would be useful to tell what kind of magnetic model is realized in the current compounds. If the authors think that there are roughly two types of J, the ones in the Kagome plane and the others that connect the plane and the interplane site, use of different color scheme will be clear.

3. In Extended Data Fig. 4, please consider using bars instead of filled triangle to indicate Bragg peak positions because of better visibility.

4. Please provide a list of the basis vectors used for each magnetic structure models in Fig.6 and Extender Data Figs.7 and 8.

5. Does the diffraction pattern allow for determining the direction of the spin moments or just relative sign between them? If the latter is the case, the direction in the drawing is redundant. I suspect that the apparently similar diffraction patterns for all the models are related to the fact that the system is nearly trigonal, which might indicate that the magnetism is roughly described by a simpler model with two types of J.

6. In Extended Data Tables 1 and 3, some justification for the fixed or same atomic displacement parameters (please use U for easier comparison) for different atoms is necessary.

7. Extended Data Table 2 is quite unorganized and needs rows and columns.

Dear Editors and Reviewers,

Thank you so much for the evaluation and comments. We have carefully considered the reviewers' comments and revised the manuscript accordingly (the revised places are marked in RED). In particular, we have successfully determined the correct magnetic structure aided by a theoretical calculation. The theoretical calculation has shown a remarkable stable total energy for one of the 8 possible magnetic structures (the model shown in Extended Data Fig. 5b in the previous manuscript) as compared to all other 7 candidates. This finally determined magnetic structure can be perfectly explained by the Cu-O-Cu super-exchange bonding, as we discussed in the revised manuscript by referring to the bonding angles in Extended Data Table 2 (we had noted the importance of the Cu-O-Cu bonding angles but hesitated to give it a decisive role in determining the magnetic structure). It turned out that the low-temperature magnetic structure is almost the same as that in the intermediate phase in Clinoatacamite in 6.0K= $T_{N2} < T < T_{N1}$ =18.1K. In Clinoatacamite we have already found that a unique up-up-down—down-down-up spin order for the neighboring triangles in the Kagome ring was formed in the $T_{N2} < T < T_{N1}$ phase in its (101) lattice plane (results reported in the annual meetings of the Physics Society of Japan and paper in preparation). For each triangle of Cu^{2+} in Clinoatacamite, the two Cu spins bonded by the smaller angle aligned parallel (up-up) while those bonded by larger angles aligned antiparallel (up-down). Although the difference in the bonding is smaller in the present pseudo-trigonal triclinic materials, the low-temperature magnetic structure in the present triclinic system turned out to be basically the same as that in the intermediate phase of monoclinic clinoatacamite. In the later, inter-kagome-layer coupling further induced transition to three-dimensional order below T_{N2}=6.0 K.

The below is a point-to-point reply list to the respective reviewer's comments.

>Reviewer #1 (Remarks to the Author):

The manuscript by X.-G. Zheng et al. analyzes a new structural polymorph of atacamite via MuSR, synchrotron-, neutron diffraction, specific heat and SQUID measurements. Observations: The synchrotron data clearly suggests a new structural modulation with notably 10 Cu sites, strengthened by the changed magnetic properties. Such a complex structure is by far no ideal system for physics. Magnetic susceptibility measurements reveal a Curie Weiß temperature of -170K, a transition is however observed around 7.5 K. In specific heat, with the given lattice contribution magnetic entropy starts to be released around 10 K, peaks at 5.5K and only reaches 20% of Rln2.The MuSR spectra are described by four components, where the

magnetic order (MO) seems to set in at 20 K, by a loss in asymmetry, but full static order is only observed at the coinciding specific heat maximum at 5.5 K. In neutron diffraction two magnetic bragg peaks were observed only at 1K, which were still absent at 9 and 30 K.Based on two visible magnetic bragg peaks refinement was done were the 6 models are basically indistuingishable. With a novel system and the given techniques it is suitable for Nature Comm. After addressing the following points the paper values publication in Nature Communications:

Thank you so much for your in-depth comment and evaluation.

1. The compound is sold as an experimental realization of the bond percolation theory in a quantum magnet based on the good agreement of 0.492(8) as a threshold compared to 2D square lattice calculations with a value around 0.593. Here other values should be compared as this is not an obvious good fit on the first glance.

It is true the previous manner of comparison to those less-related site-percolation papers may cause a wrong impression on a first glance. Since we did not find a more suitable bond-percolation magnetic work to refer, we have modified the text to avoid misunderstanding.

2. The MuSR analysis notably calls for a reinvestigation of the specific heat, as the lattice contribution seems to be captured in the temperature range of 10-22 K, while MuSR suggest that there already is magnetic contribution (at least I can see no higher T data for specific heat and it is not mentioned in the text).

To save page space by showing the magnetic specific heat in the inset plot, we sacrificed a full show of the 22K-30K specific data which could be judged from the calculated entropy line. Now we have set the inset plot as a new plot to better show the high-temperature data.

3. Indeed no magnetic bragg peaks are visible at 9 K, but given the low static ordered fraction, the signal is likely missed in the high noise.

If we see only the neutron diffraction, this might be possible. However, its sister compound clinoatacamite showed clear magnetic reflection peaks at 9 K at the same low-background beamline. And a long-range order in the 20K-5.5K with the linear increased fraction in muSR is unlikely. From those considerations, we think that the possibility of a long-range order in the intermediate range is very low even taking into consideration of the fraction. We have added discussion into the text accordingly.

4. The authors claim to have solved the Clinoatacamite mystery. However it turns out that similar to Clinoatacamite in this trigonal variant around 18 K a first onset of order occurs. In general the magnetic properties seem not too different than in Clinoatacamite. Given the synthesis technique of the system without water, a parallel to YCu3(OH)6OxCl3-x is likely (https://doi.org/10.1103/PhysRevMaterials.3.074401). Where some of the Cl is substituted by O/OH when coming in contact with water. Notably here the authors have washed their sample afterwards, so possibly a ubstitutional effect is corrected. Likely however with only powder and these many positions an occupational refinement is not feasible.

Yes, the present work alone did not completely solve the Clinoatacamite mystery. A complete understanding would be obtained by seeing our parallel study on clinoatacamite (refs. 22&23). We have reported the latter work in domestic meetings of the Physical Society of Japan (referred as references 22&23 in the manuscript) and are going to submit a formal paper shortly.

About the synthesis, as we wrote in the Methods, this compound can be also obtained in aqueous solution, but it contained impurities phases (largely of clinoatacamite), the solid reaction method helped us to succeed in pure-phase preparation. Compared with the very similar solid reaction process used in the PRM paper, still there are striking differences. In our synthesis of triclinic $Cu_4(OH)_6Cl_2$, any water must be excluded during the solid-state reaction (if water included, then a part of the powders would get oxidized causing impure phases), but after they are cooled, the compound is very steady (steady in humid air or in vacuum for over 10 years). We had carefully checked that the washing (to remove NaCl) did not change the samples' magnetic properties, neither caused any subtle change of the powder by contacting water. Reading the PRM paper, I have noted that the synthesis of $YCu_3(OH)_6O_xCl_{3-x}$ actually occurred in a controlled amount of free water, because the raw YCl_3 $6H_2O$ would dissolve to give free water before the reaction between YCl_3 $6H_2O$ and $Cu_2(OH)_2CO_3$. I guess some Cl in the x=0 $YCu_3(OH)_6Cl_3$ sample might had already been partially replaced by O due an effect arising from charge-balancing the Y^{3+}(the substitution of steadier Cu^{2+} by Y^{3+} likely to cause the structure more chemically reactive). The unstable property of the resulted $YCu_3(OH)_6Cl_3$ upon contacting moisture at room temperature seemed to support this conjecture. It might be more interesting to compare with their magnetism. The $YCu_3(OH)_6Cl_3$ in PRM showed somewhat similar magnetism below ~ 20 K but without forming a long-range order at the lowest temperature. This reminds me of the Phys. Rev. Lett. 123, 087201 (2019) paper that randomness induces spin liquid behavior, although I am not sure if the complete kagome-layer feature (the inter-kagome layer Cu being replaced by nonmagnetic Y) was a decisive factor. I am not sure if it is appropriate to give full comments to the synthesis method of $YCu_3(OH)_6Cl_3$ in the PRM, but certainly it would

be interesting to compare the magnetic order in the present compound to that in the PRM paper as we have added in the revised manuscript.

>Reviewer #2 (Remarks to the Author):

The authors studied a unique magnetic transition from short-range-ordered spin clusters into a long-range order matching the bond percolation theory in a new quantum antiferromagnet Cu4(OH)6Cl2. There are some issues that the authors need to address clearly. I suggest that they make major revisions carefully before the final decision.

Thank you very much for the assessment.

1. The author claim that intermediate magnetic order in clinoatacamite was built in its (101) lattice plane, which then was transformed by the inter-Kagome-layer couplings into a three-dimensional low-temperature spin order. What is the evidence? What is the relationship between this article and the three references cited?

We have clarified the 6.4K< T< T_{N1}=18.1K intermediate phase to be a (101) lattice plane Kagome order as we reported in two domestic meetings of the Physical Society of Japan (referred as references 22&23 in the manuscript and the Ref. 23 further reported a low-field spin flop for the kagome spins). Furthermore, to make it ambiguously clear, we have performed a wide-d range neutron experiment using the total diffractor NOVA at J-PARC in this March. Formal paper is under preparation and will be submitted shortly within one month. Since the crystal structure and magnetism of the present triclinic system and the clinoatacamite are much similar but strikingly different, it would be very interesting to compare them (If you wish to see more detailed data on clinoatacamite, we may supply some figures from the Japanese Physics Society meeting abstracts, although a full paper would be ready soon).

2. The manuscript has some spelling and grammatical mistakes. It should be thoroughly proof-read.

We have had it thoroughly proof-read.

3. How to absolutely confirm the appearance of the short-range order in the studied system? Can STEM or PDF observe more clearly?

We do not think it can be seen more clearly using STEM or PDF. STEM seems not

applicable to the powder sample and PDF would require a total diffractor wherein large background noise would be unavoidable.

4. How to comprehend the pinning effect on the magnetic transition in spin liquids?

We view the magnetic clusters in an image like magnetically ordered clusters floating in a sea of spin liquids. Since spin liquids consisted of resonating spin singlets, the growth of the short-ranged magnetic clusters would interfere with the coexisting spin liquids, i.e., have to overcome the spin liquid state to turn them into the magnetic order. Because spin liquids are strong coupled in an extensive range of space such as in the resonating spin singlets, therefore, the usually bursting quick growth of magnetic clusters would be stopped here and pinned to result a gradual and steady growth. We have modified the description in the text to give a clearer image.

5. Can theoretical calculation confirm the possible magnetic structures in Fig.6?

Thank you very much for this nice suggestion. We have asked computational physicists to join us to run DFT calculations, which have shown clear difference for these experimentally indistinguishable candidate spin structures. It turned out that the previous Extended Data Fig. 5b spin structure is much more stable and hence the correct one. For each triangle of Cu^{2+} in this magnetic structure, one bond of two spins is FM-like parallel and the remaining two pairs are antiparallel. Interestingly, all FM-like parallel spins are bonded by the smallest Cu-O-Cu angle in each triangle (as underlined in Extended Data Table 2), perfectly matching an expectation from the Cu-O-Cu super-exchange bonding. Therefore, the correct spin structure has been finally determined.

Reviewer #3 (Remarks to the Author):

Authors reported a detailed study on pseudotrigonal $Cu_4(OH)_6Cl_2$. This is an interesting study since it presents a unique magnetic system to demonstrate a complete bond percolation process toward the critical transition. The study is interesting for a wide range of readers and the related experimental results are encouraging and well explained. So, it therefore deserves publication. However, I have the following concerns:

Thank you very much for your assessment.

(1) The authors should provide the error bars for the values of parameters obtained from their measurements such as lattice parameters then the readers can have a clear idea on the accuracy of values reported. I do not believe that the accuracy for the data listed (5 digital) in Extended Data Table 1 is so high.

We have added error bars for these crystal structure parameters.

(2) In Figure 6, it is clear that two strong reflections (one at around d=5.5Å and

> around d=10Å) were not fitted well in both models, why? Moreover, the accuracy of magnetic moment looks like not correct (⊠0.08) based on the ration of signal to noise of neutron data.

They were caused by the small bin size used. They can be avoided if we use a larger bin size, but the fitting error bars would be larger. Fortunately, theoretical calculations have helped us to determine the correct spin structure, as described above.

Best Regards,

XG Zheng on behalf of all authors

Dear Editors and Reviewers,

Thank you so much for the evaluation and comments. We have carefully considered the reviewers' comments and revised the manuscript accordingly (the revised places are marked in BLUE and the previous revisions were kept in RED).

The below is a point-to-point reply list to the reviewer's comments.

> Reviewer #4 (Remarks to the Author):

>The authors report magnetic characterisation of a new triclinic polymorph of Cu2(OH)3Cl using μSR and neutron diffraction. The current manuscript lacks in clearly providing the similarity and difference in the crystal/magnetic structure, magnetic connectivity and magnetic properties between the current compound and the heavily studied polymorph, clinoatacamite, and therefore I do not think it is suitable for wide readership of Nature Communications. I also have some technical but serious concerns on the analysis of diffraction data, as below.

Thank you very much for the reviewing. Yes, these two polymorphs are unusually similar, which had been the reason for causing much confusion in the spin-liquid community despite the heavy research on clinoatacamite. But there is distinct difference in their magnetism. We have clarified their similarity and difference both in structure and magnetism. In magnetism, the low-temperature phase below 5.5 K in the present triclinic system is quite similar to the intermediate phase below T_{N1}=18.1 K in clinoatacamite: both show a 2D Kagome order [the present one in (101) Kagome lattice plane and clinoatacamite in (101) Kagome lattice plane, both of which have similar Cu-O-Cu chemical bonding]. We hope the added referring to our parallel work on clinoatacamite (recently submitted as an independent paper and already sent to nature communications as additional information for the reviewing) will help to see their difference. To avoid dual publication, unfortunately, we cannot include the data of clinoatacamite into the present paper, but we have added detailed and clearer description of the comparison in the revised manuscript. At the same time, this comparison has shown a common Kagome magnetism that should be suitable for wide readership in quantum magnetism. In particular, it is of wider interest suitable for the readership of nature communications because the present work is the first magnetic demonstration of the effectiveness of the universal percolation theory. The latter is being applied in an accelerating speed in various systems such as in chemistry, materials science, bioengineering etc. However, its effectiveness has not been demonstrated in magnetic transition-the paradigmatical one for phase transition. The geometric frustration and the unconventional stable short-range

order pinned by the coexisting spin liquids in this unique system caused a gradually developed magnetic transition process to demonstrated a complete percolation process, and the effectiveness of bond percolation theory (the critical slowing down in conventional magnetic transitions are too quick to facilitate experimental observation of the exact percolation process and threshold).

>Since the triclinic structure has not been reported elsewhere and is central to the discussion, it deserves further scrutiny. The unit cell presented in Extended Data Table 1 is close to rhombohedral symmetry in the sense that a~b~c and alpha~beta~gamma. Which peaks are new, split, or broadened in the triclinic crystal structure compared to the subgroups of R-3m, assuming that the structure derives from that of paratacamite? Le-Bail fits will be helpful to reliably determine the correct space group and subsequent analysis of the crystal structure. Unless deuteration is incomplete, it is also recommended to refine X-ray and neutron diffraction data simultaneously to obtain the hydrogen position and atomic displacement parameters of all the atoms.

Thank you very much for the suggestion. We have performed Le-Bail fits, with the peaks in both models indicated, and added a comparison in Extended Data Fig. 3 to exemplify the better fitting using the pseudo-trigonal triclinic model. Simultaneous fitting for the neutron diffraction was not possible due to the different temperatures, big difference in the sample quantity and the incomplete deuteration. However, we have added an Extended Data Table 2 for the structural data refined from the neutron diffraction. It is worth to note that (as we denoted in **Methods**) "To our surprise, this (triclinic) crystal structure has already been theoretically predicted in the Material Project (mp-1201073). It is also similar to the crystal structure previously reported for a natural mineral $Cu_{1.978}Ni_{0.028}(OH)_3Cl_{1.015}$ (36), which, however, was (wrongly) discredited as twined clinoatacamite".

>Considering the small amount of the sample used for the diffraction experiment, absence of magnetic Bragg peaks at 9 K could be just attributed to a small size of the ordered moment. Although authors states that magnetic peaks are visible in clinoatacamite at 9 K, the cited refs. 22 and 23 are unavailable. Structural refinement against the neutron powder diffraction data readily tells the ordered moment size in μB unit at 1 K, which could be compared to Fig.5d data. In order to claim that the intermediate phase is spin liquid or short-range ordered state, one should at least estimate the largest possible moment size at 9 K by comparing to the background signal.

We have added the estimated spin moments in clinoatacamite for the intermediate

phase in clinoatacamite (~0.24 and 0.39 muB for Cu1 and Cu3) and a possible limit for the triclinic system at 9 K (the spin moment at 1 K had been already provided in Fig. 6).

Best Regards,

XG Zheng on behalf of all authors

Dear Editor and Reviewer,

Thank you so much for the evaluation and comments. We have revised the manuscript accordingly (the revised places are highlighted in Green).

The below is a point-to-point reply list to the reviewer's comments.

Reviewer #4 (Remarks to the Author):

>I have listed below potential issues and suggested improvements in the revised manuscript. However, I still wonder if the finding in the triclinic polymorph would have a sufficiently broad impact.

Firstly, this is a unique magnetic transition process demonstrating the universal effectiveness of bond percolation theory in a quantum magnet. Neither experimental demonstration of the effectiveness of the universal percolation theory (the bond or site model) in magnetic transition, nor a theoretical one proving the effectiveness of the bond percolation theory have been realized so far (theoretical work only proved the effectiveness of site percolation theory in magnetic transition). And the bond percolation theory should have more wide interest in magnetism since most magnetic interactions should be via bond than via site.

Secondly, this work also has high interest in the community of frustrated magnetism and spin liquid physics (as we briefly described in the manuscript and can be also seen Ref. 18:*Reviews of Modern Physics 88 (4), 041002 (2016)*, therein our three papers on the magnetism of polymorphous $Cu_2(OH)_3Cl$, *i.e.* clinoatacamite, atacamite and botallackite were referred and the correlation between crystal structure and frustrated magnetism was fully discussed), which are also believed to be closely related to the mechanism of high-temperature superconductivity as proposed by the renown Nobel laureate Philip Warren Anderson (the RVB spin liquid model).

> Is the short-range ordered phase just above the ordering temperature in frustrated magnets so novel and surprising?

Yes, the unconventional stable static short-range ordere above the long-range ordering temperature in frustrated magnets is novel and surprising. As can be seen in the analogical case of the transition of water to ice, short-range order by far has been thought a dynamic one, and only the long-range order can be static (an exception is the random freezing in spin glass). Up to date, there is only one report of the unconventional static short-range order (Ref. 29, *Phys. Rev. B* **77**, 092403 (2008)). This work is the second case, and we have clarified the mechanism for this unusual short-range order.

> Even if some of the properties reported for clinoatacamite turned out to be those

of the current compound, what would be the significance of it, since in the end they are in the same class as the distorted pyrochlore structure? These impression might change if the authors were to describe in detail the difference in the crystal structures and show how the difference leads to the contrasting magnetic interactions and magnetic structures and the presence of the intermediate phase, but that would involve a significant change.

It has been an important question of how minimal structural difference affects the frustrated magnetism (as can be seen in the above-mentioned Ref. 18). The structural difference between the present triclinic compound, the clinoatacamite and the most-researched hot compound Herbertsmithite is small, but their magnetism is strikingly different yet sharing similarity (in particular, the present pseudo-trigonal triclinic is a rare and precious case). Since at the final stage of this work, it turned out to be the first-time demonstration of the bond percolation theory, we changed our way of writing and summarized this work in the present style. If structural correlation with spin-liquid-related frustrated magnetism were the main purpose, we should have presented this work by giving more space to this topic. We wish that the added description in the present scheme, as we have done in the revised manuscript, could solve this issue.

1. In Extended Data Fig. 3, what space groups and unit cells are used for the "trigonal" and "primitive" ones, how are they related, and what is the Miller indices of each peak? In the subgroups of R-3m and supergroups of P-1, there are five monoclinic space groups (C2/m, C2/c, P2/c, P21/c, and P21/m), and therefore these should be tested as well. This exercise might find a simpler description of the crystal structure.

We have provided analysis for all of the five monoclinic space groups in the Extended Data Fig. 5. We also added Extended Data Fig. 3 to show the peaks in three space groups. The Miller indices cannot be labelled in the plots since there are a lot of them overlapping in the monoclinic and triclinic group. We are attaching a list of these peaks in Supplementary data to reviewers for your reference.

2. Addition of magnetic connectivity in Fig.1 would be useful to tell what kind of magnetic model is realized in the current compounds. If the authors think that there are roughly two types of J, the ones in the Kagome plane and the others that connect the plane and the interplane site, use of different color scheme will be clear.

We have added magnetic structures to Fig. 1 to better show the connectivity. We believe the magnetic connectivity in the revised Fig. 1 can be clearly seen.

3. In Extended Data Fig. 4, please consider using bars instead of filled triangle to indicate Bragg peak positions because of better visibility.

This problem has been solved following your advice.

4. Please provide a list of the basis vectors used for each magnetic structure models in Fig.6 and Extender Data Figs.7 and 8.

A table of basis vectors used for each magnetic structure models has been added in the Extended Data.

5. Does the diffraction pattern allow for determining the direction of the spin moments or just relative sign between them? If the latter is the case, the direction in the drawing is redundant. I suspect that the apparently similar diffraction patterns for all the models are related to the fact that the system is nearly trigonal, which might indicate that the magnetism is roughly described by a simpler model with two types of J.

The fitting for magnetic peaks can produce directions, although they are almost along the *a*-axis. It might be better to present them in the manner you suggested (since the error bars for the *b* and *c* directions are large). Nevertheless, the theoretical calculation for final determination of the correct magnetic structure has been done with the fitted spin moments, we feel it is better to keep in this way (although the drawing in the Extended Data may seem redundant).

6. In Extended Data Tables 1 and 3, some justification for the fixed or same atomic displacement parameters (please use U for easier comparison) for different atoms is necessary.

The atomic displacements for oxygen and hydrogen only in the synchrotron X-ray Extended Data Tables 1 were fixed, which is a common practice in X-ray diffraction because of their small scattering in X-ray. We have added a justification to this table. The U is used for neutron data now. By the way, the previous Extended Data Table wrongly used the data for 1 K. Now we have replaced it with the correct 30 K data (although both produced almost equivalent results). Meanwhile, we also updated Extended Data Fig. 7|Lattice constants between 1 K – 300 K.

7. Extended Data Table 2 is quite unorganized and needs rows and columns.

We have organized them on a table.

Again, we express sincere thanks to you. We believe this second revision has further improved the presentation of our work.

Best Regards,

XG Zheng on behalf of all authors