

Experimental Consequences of Disorder at an Antiferromagnetic Quantum Phase Transition

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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)

In this manuscript, the authors have used specific heat and ac magnetic susceptibility techniques to study the field-driven quantum phase transition in antiferromagnet LiErF₄. The results reveal that the quantum phase transition in LiErF₄ can be influenced by the isotopic disorder and the deduced critical exponents from observed χ can be used to investigate the critical behavior, which is consistent with a violation of the Harris criterion in the clean regime at high-temperatures and exhibits a change in universality class in the dirty regime at low temperatures. Moreover, the unconventional power law of susceptibility at low temperatures may point to Griffiths physics and will receive more attentions to further study the paramagnetic regime. In my opinion, this is an interesting and important work. Therefore, I recommend the publication of this manuscript in Nature Communications.

However, before publishing on Nature Communications, I have some minor comments for the authors to consider.

- 1) First, it's better to give a crystal structure of LiErF₄ to Fig. 1. Second, the authors can extend the y-axis to 0 K to give a more complete evolution of AFM in the phase diagram of Fig.1.
- 2) In the phase diagram of Fig. 1, the authors don't give the information of how to define the TN. On the other hand, I suggest the authors put the TN of the specific heat measurements to Fig. 1 to further confirm the critical field.
- 3) In the results part, the authors mentioned that the critical field $H_c(T=0K) = 3645(6)$ Oe. But don't provide the information for obtaining this value. Here, I suggest the authors give some discussions on obtaining this value.
- 4) Could the authors move the information of Fig. S3 to the main text Fig. 4, which can show more clear information to the readers.

Reviewer #2

(Remarks to the Author)

The manuscript presents specific heat and ac susceptibility results on an antiferromagnet LiErF₄. The results seem consistent with those published in Science 336, 1416 (2012). However, it is unclear how this manuscript advances our understanding of novel quantum phases and phase transitions in LiErF₄ compared to that published in Science 336, 1416 (2012).

The main strength of the current paper is the specific heat results, which were reported in 2012. The previous paper reported the specific heat up to 260 mK. The current specific heat results are extended down to 55 mK; however, the low T-specific heat is dominated by contributions from nuclear Schottky and does not provide much information.

It is not clear how the system can be treated as $J_{eff}=1/2$. What is the magnetic moment at low temperature? Any estimate of the exchange interaction between Er³⁺ moments? Is there any role of disorder in the underlying exchange interactions? Quantitative and qualitative information in this context is crucial. A bit of detail regarding the crystal electric field scheme may provide interesting insights.

It is not clear how $Ah_f=6$ mK was determined. A short note on this may help the reader.

Heat capacity and specific heat in one manuscript are a bit confusing as to how the system realizes entropy $R\ln 2$. I don't find any data supporting this claim.

A bit of clarification regarding the order of the disorder may shed some insights. A short note on random mass disorder and random disorder may be helpful.

It is not clear regarding the ground state of this material as there are several predictions, such as order by disorder, field-induced quantum phase transition, and “Griffith physics,” without much evidence and discussion.

There are several statements without much discussion or experimental evidence. For instance, it is not clear what the author wants to convey with the sentence “Varying the importance of disorder...”

Overall, the manuscript doesn't stand on its own. I don't recommend the manuscript for publication in Nature Communications in the present form.

Reviewer #3

(Remarks to the Author)

The authors present an experimental study of phase transition in antiferromagnetic compound LiErF₄. Measuring various critical exponents near the transition from heat capacity and magnetic susceptibility data, they conclude that random mass disorder arising from the nuclear spin moments plays an important role in determining the universality class of the transition.

Before going to my overall impression regarding the manuscript, I would like to convey my comments and suggestions regarding this work.

1. Throughout the presentation, the authors give estimates of various critical exponents and compare it with the already known results of various universality classes. For a better readership, it would be nice if this information is presented in a tabulated concise form.
2. In line 84-85, authors mention the possibility of new degrees of freedom at low energy scales based on the unusual thermal broadening at low temperatures. The authors should be more precise about which excitations they are referring to. It is not clear whether these excitations are related to the magnetic ordering or electronuclear coupling.
3. The authors suggest that the electronuclear coupling is particularly strong at low temperatures and can have a strong effect of changing the universality class. However, from the specific heat data below critical temperature, the electronic and nuclear contributions to the specific heat remain additive. This seems a contrast to the claim of emergence of disorder-induced electronuclear excitations.

Overall, I appreciate the concise approach of the work giving the experimental support for the theoretical predictions about the effect of random mass disorder on quantum critical points. The manuscript is well-written and well-organized. It nicely gives concise review of important piece of theoretical results to guide the readers. Understanding the role of disorder on strongly correlated systems has been a major challenge to the community, and this work perfectly serves that purpose. However, the authors should address the above critical comments for better clarity of the draft. I would like to recommend the work to be published in nature communications upon addressing the above concerns.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have properly addressed all the concerns of referees, and I suggest that the manuscript can be considered for publication.

Reviewer #2

(Remarks to the Author)

The substantially revised manuscript may be considered for publication in Nature Communications.

Reviewer #3

(Remarks to the Author)

The authors have addressed the suggestions and improved the manuscript accordingly. I am happy to recommend its publication in nature communications in its present form.

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REVIEWER COMMENTS

Before addressing the specific concerns of the Reviewers, we point out a systematic shift in temperature scales between the original version of the manuscript and this revised version. In the interim, we identified an issue with the calibration table for the thermometer supplied with the PPMS Dilution Refrigerator used for all of the measurements reported in the manuscript. The discrepancy (3 mK at 50 mK, 15 mK at 300 mK) was quantified by comparing the built-in thermometer with an additional thermometer calibrated in a different cryostat against a NIST-traceable Lake Shore RX-102B reference thermometer. The temperatures shown in the figures and given in the text have been corrected and none of the conclusions presented in the manuscript have been affected.

Reviewer #1 (Remarks to the Author):

In this manuscript, the authors have used specific heat and ac magnetic susceptibility techniques to study the field-driven quantum phase transition in antiferromagnet LiErF₄. The results reveal that the quantum phase transition in LiErF₄ can be influenced by the isotopic disorder and the deduced critical exponents from observed χ_c can be used to investigate the critical behavior, which is consistent with a violation of the Harris criterion in the clean regime at high-temperatures and exhibits a change in universality class in the dirty regime at low temperatures. Moreover, the unconventional power law of susceptibility at low temperatures may point to Griffiths physics and will receive more attentions to further study the paramagnetic regime. In my opinion, this is an interesting and important work. Therefore, I recommend the publication of this manuscript in Nature Communications.

However, before publishing on Nature Communications, I have some minor comments for the authors to consider.

1) First, it's better to give a crystal structure of LiErF₄ to Fig. 1. Second, the authors can extend the y-axis to 0 K to give a more complete evolution of AFM in the phase diagram of Fig.1.

We thank Reviewer 1 for their suggestions on improving Fig. 1. We have added to Fig. 1 a panel depicting the full crystal structure of LiErF₄ and extended the y-axis of the phase diagram to T=0.

2) In the phase diagram of Fig. 1, the authors don't give the information of how to define the T_N .

We thank Reviewer 1 for noting this omission. This information has been added to the caption of Fig. 1.

On the other hand, I suggest the authors put the T_N of the specific heat measurements to Fig. 1 to further confirm the critical field.

The Reviewer is correct in identifying the specific heat measurements as an additional check of the accuracy of our phase boundary. However, we note two complications in making a direct comparison between the specific heat measurements and the susceptibility measurements presented in Fig. 1.

- (1) The plate-like sample dimensions ($1 \times 1 \times 0.04 \text{ mm}^3$) necessary to perform specific heat on a single-crystal insulator at mK temperatures results in a significantly larger demagnetization field which increases the effective critical field. This effect was quantified in the sample methods subsection, where we compare susceptibility for needle and plate geometries cut from the same parent crystal.
- (2) The nuclear-spin Schottky contribution to the specific heat becomes dominant at temperatures below $T=150 \text{ mK}$ and obscures the peak associated with magnetic ordering.

We believe that these subtleties would distract from the points of the main text.

3) In the results part, the authors mentioned that the critical field $H_c(T=0\text{K}) = 3645(6) \text{ Oe}$. But don't provide the information for obtaining this value. Here, I suggest the authors give some discussions on obtaining this value.

We find the critical field by fitting the phase boundary to a power law form. This fitting form is valid when T_N is proportional to the order parameter. We found agreement between this power law description and the order parameter measurements reported in Science **336**, 1416 (2012). The results section (page 4) has been updated to include a description of the fit:

"A critical field of $H_c(T=0)=3645(6) \text{ Oe}$ is found by fitting the phase boundary to a power law form."

4) Could the authors move the information of Fig. S3 to the main text Fig. 4, which can show more clear information to the readers.

We have included the information of Fig. S3 by adding it as a third panel to Fig. 4 and have edited the text and caption of Fig. 4 accordingly.

Reviewer #2 (Remarks to the Author):

The manuscript presents specific heat and ac susceptibility results on an antiferromagnet LiErF₄. The results seem consistent with those published in Science 336, 1416 (2012). However, it is unclear how this manuscript advances our understanding of novel quantum phases and phase transitions in LiErF₄ compared to that published in Science 336, 1416 (2012).

Our work builds on the results of Science 336, 1416 (2012) in several key ways:

- We take field sweeps rather than temperature sweeps of magnetic susceptibility. This allows us to identify the existence of a high temperature “clean” regime and a low temperature disordered regime, and to quantify the effects of disorder on the quantum critical behavior.
- We extend specific heat measurements down to 58 mK. Data down to these temperatures is needed to demonstrate that the transition temperature between the two regimes coincides with the nuclear spins slaving to the electronic spins.
- We discuss the magnetic susceptibility as a control parameter susceptibility. In doing so, we are able to relate the critical behavior to the Harris Criterion.

The main strength of the current paper is the specific heat results, which were reported in 2012. The previous paper reported the specific heat up to 260 mK. The current specific heat results are extended down to 55 mK; however, the low T-specific heat is dominated by contributions from nuclear Schottky and does not provide much information.

The Schottky contribution is a direct measurement of and sets the energy scale for isotopic disorder. Its effects lead to anomalous behavior in the magnetic susceptibility and change the universality class of the quantum phase transition. These substantive elements of the physics are only revealed because of the factor of five lower temperatures reached in the present experiment.

It is not clear how the system can be treated as $J_{\text{eff}}=1/2$. What is the magnetic moment at low temperature?

The description of the system as spin-1/2 follows from the procedure first outlined in Phys Rev. B **70**, 144411 (2004) for LiHoF₄ and later applied to LiErF₄ in Science **336**, 1416 (2012). The procedure is as follows:

1. Diagonalize the single-ion Hamiltonian of Er (the crystal field and Zeeman term).
2. Form an effective Hamiltonian from the subspace spanned by the single-ion ground state doublet.
3. Project the full $J=15/2$ spin operators into this subspace to find how the electronic moment is renormalized. This information is encoded in the effective g-factors in the spin-1/2 subspace.
4. Substitute the full spin operators with the truncated spin operators into the dipolar interaction.

This approximation is valid for spin systems with a ground state doublet over a temperature range which is much smaller than the gap to the first excited state. For LiErF₄, the gap to the first excited state is ~26 K. This is approximately 2 orders of magnitude above the temperature range of this work.

Any estimate of the exchange interaction between Er³⁺ moments?

We are unaware of any measurements of the exchange interaction between Er³⁺ moments; however, it is expected to be much smaller than the dipolar interaction given the 4f nature of the Er ions. The exchange energy for the Ho³⁺ moments in LiHoF₄ was reported as $J_{\text{ex}} = 1.16$ mK in Phys. Rev. B **75**, 054426 (2007). We expect a similar energy scale for the exchange interaction between Er³⁺ moments, which is negligible relative to the dipolar interaction.

Is there any role of disorder in the underlying exchange interactions?

The exchange interaction is only dependent on the electronic degrees of freedom of the system, which are free from disorder.

Quantitative and qualitative information in this context is crucial. A bit of detail regarding the crystal electric field scheme may provide interesting insights.

The effects of the crystal electric field relevant to the temperature scale of interest are fully captured by the effective g-factor. We have added a note to page 2 of the manuscript to make this point clearer:

“The crystal field induces strong easy plane anisotropy which, within the effective subspace, is fully described by an anisotropic g-factor $(g_{\perp} / g_{\parallel})^2 = 13.8$.”

It is not clear how $A_{hf}=6$ mK was determined. A short note on this may help the reader.

We reference the hyperfine coupling strength reported in Phys. Rev. B **4**, 1 (1971). This value was determined by electron-paramagnetic-resonance spectroscopy. We have added a note in the text for clarity (page 3):

“A coupling strength of $A_{hf}=6$ mK was found by electron-paramagnetic-resonance spectroscopy.”

Heat capacity and specific heat in one manuscript are a bit confusing as to how the system realizes entropy $R \ln 2$. I don't find any data supporting this claim.

We thank reviewer 2 for identifying our inconsistent use of the terms heat capacity and specific heat. The text has been edited to only use specific heat.

To determine the electronic-spin entropy, we first subtract away the nuclear spin Schottky contribution to isolate the purely electronic spin specific heat. We then integrate the electronic specific heat from 58 mK (where it is within error bars of zero) to 4 K. We have added a supplementary figure which shows this calculation and compares it with the expected $R \ln 2$.

A bit of clarification regarding the order of the disorder may shed some insights. A short note on random mass disorder and random disorder may be helpful.

We have added a note (page 9) explaining why the isotopic disorder falls within the category of random mass disorder:

“Since the isotopic disorder in our system does not break local symmetry, it falls within the category of random mass disorder, and the Harris criterion is applicable.”

It is not clear regarding the ground state of this material as there are several predictions, such as order by disorder, field-induced quantum phase transition, and “Griffith physics,” without much evidence and discussion.

As depicted in Fig. 1, the low-field ground state is a bilayer antiferromagnet. Above H_c , the ground state is a paramagnet. We have altered the introduction to make clear that the high field ground state is a paramagnet.

Order by disorder is not a ground state. It is a mechanism by which fluctuations lift the degeneracy in a material's free energy and cause order. This mechanism was proposed in

Science 336, 1416 (2012) to describe the experimentally observed anisotropy within the a-b plane.

We have added a note to the supplementary section outlining the relevance of Griffiths physics and how it could be experimentally investigated:

“Near the QPT, rare spatial regions with a low concentration of disorder favor local ordering. Whether these regions contribute to the bulk thermodynamics of the system is dependent on d_{RR} , the dimensionality of correlation in the disorder, and d_c^- , the lower critical dimension of the spin symmetry. In the case of an Ising QPT with random disorder, $d_c^- = 1$, and $d_{RR} = 1$ because disorder is correlated in the imaginary time dimension. This equality corresponds to an infinite-randomness quantum critical point. This QPT is predicted to have a non-universal α_T that varies with the tuning parameter and approaches 1 at the QPT. This has been observed experimentally in some materials; however, in many cases an exponent less than one is observed at the QPT. We suggest Griffiths physics as a possible explanation for the unconventional exponent, $\alpha_T = 0.70$, reported for LiErF₄.”

There are several statements without much discussion or experimental evidence. For instance, it is not clear what the author wants to convey with the sentence “Varying the importance of disorder...”

We have edited the text (page 2) to make our point clearer.

“A thorough experimental investigation of the role of disorder in phase transitions requires probing the system at various strengths of that disorder. Typically, randomness is introduced by a structural or compositional mechanism that entails studying a sequence of separate samples over a range of disorder, which can be difficult to synthesize controllably”

Overall, the manuscript doesn't stand on its own. I don't recommend the manuscript for publication in Nature Communications in the present form.

Reviewer #3 (Remarks to the Author):

The authors present an experimental study of phase transition in antiferromagnetic compound LiErF₄. Measuring various critical exponents near the transition from heat capacity and magnetic susceptibility data, they conclude that random mass disorder arising from the nuclear spin moments plays an important role in determining the universality class of the transition.

Before going to my overall impression regarding the manuscript, I would like to convey my comments and suggestions regarding this work.

1. Throughout the presentation, the authors give estimates of various critical exponents and compare it with the already known results of various universality classes. For a better readership, it would be nice if this information is presented in a tabulated concise form.

We thank reviewer 3 for their suggestion. We have added a table to the supplementary section which lists the exponents of the classical and quantum phase transitions of LiErF_4 and the mean field, 2D Ising, 3D Ising, 3D XY, and 2D XY/h4 models.

2. In line 84-85, authors mention the possibility of new degrees of freedom at low energy scales based on the unusual thermal broadening at low temperatures. The authors should be more precise about which excitations they are referring to. It is not clear whether these excitations are related to the magnetic ordering or electronuclear coupling.

We thank reviewer 3 for identifying a need for clarification in this section. When considering a single energy scale, broadening due to thermal effects should decrease monotonically. The non-monotonic nature of the broadening provides evidence for the presence of a second energy scale. Since the higher energy scale is known to be from a purely electronic origin, we can deduce that there is an excitation with an electronic coupling that has a strength of the order of this lower energy scale. We use specific heat measurements to determine the nature of this new excitation. The text has been edited to make this point more clearly (page 4):

“In a conventional description of a QPT with a single energy scale, monotonic thermal broadening is expected and can be understood as a finite size effect in the imaginary time dimension.¹⁸ The unexpected broadening in the low temperature regime suggests the presence of a second energy scale that is not electronic in origin.”

3. The authors suggest that the electronuclear coupling is particularly strong at low temperatures and can have a strong effect of changing the universality class. However, from the specific heat data below critical temperature, the electronic and nuclear contributions to the specific heat remain additive. This seems a contrast to the claim of emergence of disorder-induced electronuclear excitations.

The Schottky behavior we see in our specific heat measurements describes a nuclear spin aligning with a constant magnetic field as temperature is decreased. The dominant magnetic field present at the nucleus of an Er ion is due to its 4f electronic cloud. This field

will not be affected by the nuclear spin slaving to the electronic spin, so the specific heats from each degree of freedom will remain additive.

Overall, I appreciate the concise approach of the work giving the experimental support for the theoretical predictions about the effect of random mass disorder on quantum critical points. The manuscript is well-written and well-organized. It nicely gives concise review of important piece of theoretical results to guide the readers. Understanding the role of disorder on strongly correlated systems has been a major challenge to the community, and this work perfectly serves that purpose. However, the authors should address the above critical comments for better clarity of the draft. I would like to recommend the work to be published in nature communications upon addressing the above concerns.