Observation of chiral solitons in LiCuVO_4

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Quantum spin liquids represent a magnetic ground state arising in the presence of strong quantum fluctuations that preclude ordering down to zero temperature and leave clear fingerprints in the excitation spectra. While theory bears a variety of possible quantum spin liquid phases their experimental realization is still scarce. Here, we report experimental evidence for chiral solitons in the $S = 1/2$ spin chain compound LiCuVO_4 from measurements of the complex permittivity ϵ^* in the GHz range. In zero magnetic field our results show short-lived thermally activated chiral fluctuations above the multiferroic phase transition at $T_N = 2.4$ K. In ϵ^* these fluctuations are seen as the slowing down of a relaxation with a critical dynamical exponent $\nu_{\epsilon} \approx 1.3$ in agreement with mean-field predictions. When using a magnetic field to suppress T_N towards 0 K the influence of quantum fluctuations increases until the thermally activated fluctuations vanish and only an excitation can be observed in the dielectric response in close proximity to the phase transition below 400 mK. From direct measurements we find this excitation's energy gap as $E_{SE} \approx 14.1 \mu\text{eV}$, which is in agreement with a nearly gapless chiral soliton that has been proposed for LiCuVO_4 based on quantum spin liquid theory.

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In solid-state physics, unique phenomena emerge when a long-range order is suppressed by an external parameter towards lower temperatures where quantum fluctuations dominate. This suppression often reveals a ‘dome’-like new phase at the bottom of a conical cross-over region and a significant change of the critical dynamics¹. Famous examples for this are superconductivity^{2,3}, heavy fermion systems^{4,5}, and quantum spin liquids⁶, all of which are accompanied by changes of the excitation spectra. To investigate the influence of quantum fluctuations on the critical dynamics, systems with low dimensionality are a good starting point as they ideally do not order even at $T \rightarrow 0$ K. Experimentally, strictly 1D systems are, of course, not available, but systems where the magnetic ions are located on structures with lower dimensionality, e.g., spin-chain compounds, have been shown to undergo magnetic field-driven phase transitions at very low temperatures. As these quantum phase transitions are driven by quantum fluctuations and not by temperature unusual dynamics are expected to emerge in their proximity. The influence of quantum fluctuations is even stronger when the systems have almost isotropic spin $S = 1/2$ in so-called Heisenberg spin chains. One way to introduce vector spin chirality in such a spin chain is frustration due to competing nearest and next-nearest neighbor interactions, J_1 and J_2 , in the presence of a small easy-plane anisotropy^{7,8}. Apart from being chiral, these phases can be magnetoelectric multiferroic^{9,10} as has been observed in many compounds^{11,12}. The coupling between magnetization M and polarization P has potential applications for data storage^{13,14} and, most important for this work, it allows to observe the dynamics of the magnetic system via measurements of the polarization dynamics^{15,16}. In particular, in the case of magnetoelectric multiferroics an electromagnon^{17,18}, i.e., collective magnetic excitations that also carry electric polarization, can be observed. The corresponding fluctuation dynamics show critical slowing down at the multiferroic phase transition¹⁹ that can be tuned towards $T \rightarrow 0$ K in an external magnetic field. Close to this quantum critical point a change in the fluctuation dynamics can be observed via dielectric measurements²⁰. It has also been shown, that quantum critical behavior can be observed above the critical point that terminates a first-order phase transition²¹.

Here, we report experimental evidence for a chiral quantum spin-liquid state in LiCuVO_4 . This evidence is based on the analysis of the T -, H -, and ν -dependence of the complex permittivity ϵ^* of LiCuVO_4 close to the multiferroic phase transition down to 0.025 K with frequencies in the GHz range. Our results show classical critical slowing down at the multiferroic phase transition with a critical dynamical exponent $\nu_{\xi z} \approx 1.3$ above 1.0 K in agreement with mean-field predictions¹⁵. For an external magnetic field, the transition is shifted towards low temperatures. In close proximity to the multiferroic phase transition, we observe both quantum critical slowing down of the fluctuations as well as the emergence of a nearly gapless excitation that is in agreement with the chiral soliton proposed for LiCuVO_4 in⁸ based on quantum spin-liquid theory. From direct measurements, we find an energy gap of $E_{\text{SE}} \approx 14.1 \mu\text{eV}$ for this excitation.

Results and discussions

LiCuVO_4 has a distorted inverse spinel-type structure²², see Fig. 1a. Here, a low-dimensional spin system is realized by Cu^{2+} ions with $S = 1/2$ that form 1D chains along the b axis separated in a direction by VO_4 tetrahedra and by Li along the c direction. Competing ferromagnetic $J_1 < 0$ and antiferromagnetic $J_2 > 0$ interactions²³ lead to frustration along the spin chains and cycloidal Néel ordering of the spins within the ab plane is observed below $T_N = 2.4$ K due to weak interchain coupling, as sketched in Fig. 1b. In this phase, LiCuVO_4 is multiferroic with an

electric polarization $\mathbf{P} \propto \mathbf{k} \times (\mathbf{S}_i \times \mathbf{S}_{i+1})$ parallel to the a axis. By applying a magnetic field along the c axis the 3D order can be weakened and T_N is continuously suppressed down to 0 K at $\mu_0 H_c \approx 7.4$ T^{16,24,25}, raising the question if a quantum phase transition occurs.

A characteristic signature of pressure-dependent quantum phase transitions^{26,27}, that is observed in various quasi-1D quantum spin materials^{28–33}, is a sign change of the Grüneisen ratio $\Gamma = \alpha_i/C_p$ (with the uniaxial thermal expansion coefficient α_i and the specific heat $C_p > 0$) close to H_c . Below H_c , the transition into the multiferroic phase causes sharp anomalies in $\alpha_i = 1/L \partial L / \partial T$ (i denotes the orthorhombic axes a, b, c), as is shown for 7.0 T (red) in Fig. 1c–e. Upon increasing the magnetic field $H||c$ above H_c , these anomalies vanish and α_i changes sign for each axis i . Note that the sign change of α_a occurs above 7.5 T, which may arise either from a stabilization of the multiferroic phase for uniaxial pressure along a and/or from a slight misorientation of the magnetic field. Experimentally, magnetic field-dependent measurements are more reliable when the phase boundary is very steep close to H_c , see Fig. 1b. Therefore, we measured the magnetic field-dependent Grüneisen parameter $\Gamma_H = 1/T \partial T / \partial (\mu_0 H)$, which is obtained from the ratio of the magnetocaloric effect and C_p ^{32,33}, that confirms the sign change (Fig. 1f).

Based on coexisting phases neutron scattering experiments suggest that the field-driven phase transition is of first-order at very low temperatures^{34,35}. However, there are no indications of hysteresis effects in any of our measured macroscopic quantities. In combination with the observed quantum critical behavior, we propose that the first-order transition at very low temperatures changes at a critical point into a second-order phase transition. This could be a Lifshitz point³⁶ which separates the low-field cycloidal phase with constant wave vector q from the spin-modulated phase with a varying $q(H)$ ^{34,35}. In this case, the quantum critical behavior also ends at the critical point and not at $T=0$ K as discussed e.g., for the critical end point in $\text{Sr}_3\text{Ru}_2\text{O}_7$ ²¹.

When increasing the magnetic field above H_c at low temperatures the system enters a collinear spin-modulated phase with short-range order^{35,37} and vector-chiral correlations were reported to exist already for $T > T_N$ ³⁸. Above 41 T, LiCuVO_4 enters a spin-nematic phase and a saturated phase above 44 T³⁹, both of which are well beyond the magnetic field range used in this work.

The multiferroic phase transition can not only be observed in thermodynamic quantities, but also in dielectric spectroscopy. As this technique also measures a background of regular phonon contributions we subtracted measurements away from the phase transition to isolate the additional multiferroic contribution $\Delta\epsilon^*$ close to the phase transition.

Thermally activated fluctuations. On approaching the multiferroic phase transition, thermally activated chiral fluctuations appear already above T_N whose size and lifetime diverge for $T \rightarrow T_N$. In this regime dispersion is observed in $\Delta\epsilon'$, see Fig. 2a, as the high frequencies break away from the quasi-static response that is given by the envelope of $\Delta\epsilon'$ (dashed line). This behavior is accompanied by corresponding contributions in the dielectric loss $\Delta\epsilon''$ at temperatures above T_N shown in Fig. 2b. These characteristic features of a phonon mode's critical slowing down are expected in both ferroelectric as well as multiferroic materials¹⁵. As a well-founded expectation for these results already exists we can use the fluctuations to both demonstrate the viability of the background correction as well as introduce the classical effects that overlay the quantum fluctuation effects discussed later on. To quantify the dynamics above the phase transition we utilize critical dynamical scaling that relates the relaxation time $\tau \propto \xi^z$ to the correlation length ξ via the dynamical exponent z . Close to

Fig. 1 Introduction of LiCuVO₄. **a** A fraction of the crystal structure of LiCuVO₄ (data from ref. ²³), the ordered magnetic moments of Cu in the multiferroic phase are indicated. **b** A sketch of the temperature (T) vs magnetic field ($\mu_0 H$) phase diagram. The pre-factor of H is the vacuum permeability $\mu_0 = 4\pi \cdot 10^{-7} \text{ Vs(Am)}^{-1}$. **c–e** The temperature-dependent thermal expansion coefficients α_i for all three crystallographic axes change sign once the external magnetic field crosses the critical magnetic field $\mu_0 H_c \approx 7.4 \text{ T}$, and **f** an analogous sign change occurs in the magnetic field-dependent measurements of the magnetic Grüneisen parameter $\Gamma_H = 1/T \partial T / \partial (\mu_0 H)$.

the phase transition the correlation length ξ diverges, $\xi(T) \propto |T/T_N - 1|^{-\nu_{\xi,T}}$, with the positive correlation length exponent ν_{ξ} . Therefore, we look at the permittivity in the frequency domain where $\varepsilon^*(\nu)$ is described by a Debye relaxation

$$\varepsilon_{\text{EM}}^*(\nu) = \frac{\Delta\varepsilon_s}{1 - i2\pi\nu\tau}. \quad (1)$$

with the step height $\Delta\varepsilon_s$ in ε' and the relaxation time τ . In Fig. 2e the complex permittivity is shown for different temperatures as both, $\varepsilon'(\nu)$ (circles) and $\varepsilon''(\nu)$ (triangles) with fits of the Debye relaxation (lines). Here, the arrows mark the position $\nu_p = 1/2\pi\tau$ of the maxima in the dielectric loss, and their shift towards lower frequencies upon cooling demonstrates the critical slowing down close to the phase transition. Additional information on the dynamics can be gained from the height of the step $\Delta\varepsilon_s$. According to the Lyddane–Sachs–Teller relation⁴⁰ the mode's eigenfrequency ω_{EM} is connected to the critical increase in the static permittivity by $\Delta\varepsilon_s \propto \omega_{\text{EM}}^{-2}$. As relaxation is characterized by high damping $\omega_{\text{EM}}^2 \approx \Gamma_{\text{EM}}/\tau$ holds and $\Delta\varepsilon_s$ is therefore also proportional to τ . In Fig. 2g we show that a critical exponent $\nu_{\xi,T} \approx 1.3$ simultaneously describes $\nu_p = 1/2\pi\tau$ and $1/\Delta\varepsilon_s$ when choosing the position of the maximum for the lowest frequency as T_N . This result is in agreement with the expectation of $\nu_{\xi,T} \approx 1.272$ for materials of the 3D-Ising universality class¹⁵.

At the steep phase boundary close to H_c we performed measurements of $\Delta\varepsilon(\nu, H)$ at constant T . Compared to $\mu_0 H = 0 \text{ T}$ the feature at $T = 1.0 \text{ K}$ is slightly smaller as the spins are canted

into the direction of the magnetic field and, thus, reducing $\mathbf{P} \propto \mathbf{k} \times (\mathbf{S}_i \times \mathbf{S}_{i+1})$, see Fig. 2c, d. The observed dynamics, on the other hand, are almost identical and also show critical slowing down, as seen in the spectra in Fig. 2f. Evaluating the critical exponent from ν_p and $\Delta\varepsilon_s$, in this case its magnetic field dependence $\tau(H) \propto |H/H_c - 1|^{-\nu_{\xi,H}Z}$ with H_c again from the maximum at the lowest frequency, yields $\nu_{\xi,H}Z \approx 1.3$, also in agreement with the expected mean-field behavior¹⁵.

Dynamics from quantum fluctuations. Below 1.0 K we observe a fundamental change in the fluctuation dynamics in both, the permittivity $\Delta\varepsilon'$ shown in Fig. 3a and the dielectric loss $\Delta\varepsilon''$ in Fig. 3b. In $\Delta\varepsilon'$ the dispersive peak from temperature-activated fluctuations evolves into an up to $\approx 1 \text{ GHz}$ dispersionless maximum at H_c . In the dielectric loss, a corresponding peak is only visible in a narrow frequency range between 2 and 3 GHz. This missing low-frequency contributions in $\Delta\varepsilon''$ indicate, that excitation with low damping is observed at lowest temperatures. While the observed absolute value of the permittivity depends on H and vanishes outside of $6.5 \text{ T} \lesssim H \lesssim 8 \text{ T}$, within the experimental accuracy the observed excitation shows the same frequency dependence for all magnetic fields within this magnetic field range. Therefore, we only discuss the data close to H_c .

To examine the change in the fluctuation dynamics in more detail we again look at the data in the frequency domain. The excitation observed at the lowest temperatures is taken into

Fig. 2 T- and H-dependent critical dynamics of thermally activated fluctuations. Real and imaginary part of the complex permittivity in the frequency range of 56 MHz–5.6 GHz from temperature (T) dependent measurements in zero magnetic fields are shown in **a**, **b** and magnetic field (H) dependent measurements at 1.0 K are shown in **c**, **d**. Contributions of faster polarization effects have been subtracted. In **e**, **f** the measured permittivity spectra (circles for $\Delta\epsilon'(\nu)$ and triangles for $\Delta\epsilon''(\nu)$) are shown with the fitted Debye relaxation as solid lines for the T – and H – dependent measurements respectively. Here, the spectra are offset for enhanced visibility and the peak positions in the dielectric loss are marked by arrows. The T – (in **g**) and H – dependence (in **h**) of the parameters ν_p and $1/\Delta\epsilon_s$ can be described with a critical dynamical exponent of 1.3. The error bars in **g**, **h** represent the root mean squared error obtained for the fits of the Debye relaxations.

account by adding a Lorentz oscillator with the plasma frequency ω_p , the undamped eigenfrequency ω_0 , and the damping Γ to eq. (1):

$$\epsilon^*(\nu) = \epsilon_{EM}(\nu) + \frac{\omega_p^2}{\omega_0^2 - (2\pi\nu)^2 + i2\pi\nu\Gamma}. \quad (2)$$

The real and imaginary part of $\epsilon^*(\nu)$ are shown for several temperatures and constant magnetic field $\mu_0 H = 7.4$ T, i.e., close to H_c in Fig. 4a, b. The results of the fits are shown as solid lines in both panels and are in good agreement with the data, the two individual processes are shown as gray (relaxation) and blue (excitation) dashed lines. A single relaxation process is sufficient to describe the data at 1.0 K, both processes are needed in an intermediate temperature regime until only the excitation remains below 0.2 K.

For the relaxation, the shift towards lower frequencies on cooling again indicates critical slowing down. In contrast to the previously discussed case of thermally activated fluctuations,

these measurements were taken within the quantum critical regime and a different critical scaling is observed. The temperature dependence of the peak frequencies $\nu_p(T)$, shown as gray dots in Fig. 4c, follows a critical exponent of $\nu_{\xi,T} \approx 2$ (solid line) which was also observed for multiferroic $\text{Ba}_2\text{CoGe}_2\text{O}_7$ ²⁰. Different from this material, the temperature of the critical point $T_{cp} \approx 0.37$ K has to be taken into account in LiCuVO_4 when discussing the slowing down of the quantum fluctuations.

In contrast to the relaxation, the excitation does not show critical slowing down upon cooling, but instead its maximum shifts to higher frequencies, as shown as blue dots in Fig. 4c. This apparent “speeding up”⁴¹ can be explained by a reduced damping Γ with decreasing T , plotted as triangles in the figure, while the eigenfrequency ω_0 is independent of temperature. As this excitation is observed with dielectric spectroscopy the underlying mechanism has to include electric polarization. Therefore, the type of excitation, namely the stimulation via an electric field, demonstrates that we are not dealing with simple spin dipolar

Fig. 3 Low-temperature dielectric measurements. The magnetic field-dependent complex permittivity $\Delta\epsilon^*$ in the vicinity of H_c for different frequencies and temperatures. In **a** the evolution of $\Delta\epsilon'$ from a dispersive feature at a higher temperature into a peak with no dispersion up to approximately 1 GHz (green) with a steep drop above this frequency with cooling is shown. The dielectric loss $\Delta\epsilon''$ in **b** also changes from a broad, dispersive maximum at higher temperatures observed for all frequencies to **a**, in the frequency domain, a narrow peak located roughly between 2 and 3 GHz at low temperature.

Fig. 4 Dynamics at low temperatures. Measured spectra (points) of the complex permittivity $\Delta\epsilon^*(\nu)$ at $H \approx H_c$ with fits of Equation (2) (lines) are shown in **a** for the real part, $\Delta\epsilon'$, and the imaginary part, the dielectric loss $\Delta\epsilon''$, in **b** as a function of the frequency ν . The fitted peak frequencies of the maxima in $\Delta\epsilon''$ are shown in **c** for both the relaxation (gray squares) and the emergent excitation (blue circles) on the left scale with the corresponding damping factor for the excitation (triangles) on the right scale. The error bars in **c** correspond to the root mean squared error that was obtained when fitting the spectra with Equation (2).

Fig. 5 Chiral solitons. **a** The pristine spin chain with uniform clockwise vector handedness. Dimers are marked by colored backgrounds to differentiate between the alternating species that make up the uniform spin chain. **b** By flipping both spins in a dimer it transforms into the other species and two chiral solitons are created. This process is slightly gapped due to the presence of interchain coupling in LiCuVO_4 . **c** By exchanging two neighboring dimers the soliton can move through the spin chain without creating additional changes in its handedness. Based on ref. ⁸.

fluctuations but with magnetoelectric, vector-chiral fluctuations. This also excludes the bimagnon excitation proposed in LiCuVO_4 ³⁵ because the bimagnon excitation should stem from a collinear spin arrangement and this would not carry an electric dipole moment. Thus, our experimental results show the existence of chiral solitons and thereby support the occurrence of a chiral spin-liquid state close to H_c as has been predicted in ref. ⁸.

Chiral solitons. In a theoretical work by Furukawa et al.⁸ it has been shown that quantum fluctuations in frustrated $S=1/2$ systems can lead to the emergence of a spin-liquid state in which the spins dimerize. The characteristic excitations of this state are chiral solitons that are proposed to work as follows⁸: starting from a uniform spin chain in Fig. 5a the suppression of long-range order leads to dimerization. To enhance visibility neighboring dimers in the uniform spin chain are highlighted with alternating dashes in green and blue that have almost inverted spin orientations. In the beginning, the vector handedness of the spiral and, therefore, its polarization is uniform, here clockwise. By flipping both spins in a dimer it changes its “type”, here from blue to green, see Fig. 5b. During this process, two defects in the as yet uniform chirality of the spin chain are created, that are marked in red, and cause a local flip of the electric dipole moment. By exchanging neighboring dimer pairs these chiral solitons can move through the spin chain, e.g. in opposite directions with effective $q=0$, see Fig. 5c. While the model used by Furukawa et al. does not explicitly use an external magnetic field it has been shown⁷ that despite magnetic fields perpendicular to the easy plane the vector-chiral state remains for small magnetic fields and can also be present in the $U(1)$ symmetric case.

Due to the change in the chirality, the soliton’s electric dipole moments locally point against the ferroelectric background of the uniform spin chain and they are thus visible by dielectric spectroscopy. For LiCuVO_4 these excitations have been predicted to be slightly gapped due to interchain coupling, which is in perfect agreement with our results. We find that the gap of the soliton excitation is indeed very small, $\omega_0/2\pi \approx 3.4$ GHz which corresponds to a gap energy of $E_{\text{SE}} = 14.1$ μeV .

The chiral solitons are not only observed close to the first-order phase transition where the 3D order is weakened. Above the critical point, the chiral solitons can be observed as long as the lifetime of the quantum fluctuations is larger than the inverse peak frequency of the excitation, $\tau_{\text{EM}} > 1/\omega_0$. At higher temperatures, the lifetime of the fluctuations decreases and the damping

increases, such that the chiral solitons become too broad to be observed.

Conclusions. Our measurements of the complex permittivity close to the multiferroic phase transition in LiCuVO_4 demonstrate the changing polarization dynamics in the presence of increasing quantum fluctuations. At temperatures above 1.0 K we see the mean-field behavior expected for the critical dynamics at a multiferroic phase transition: critical slowing down for both, the temperature and magnetic field-dependent measurements. When T_N is suppressed further the critical slowing down of thermal fluctuations is insufficient to describe the dynamics. Instead, thermal and quantum fluctuations compete until the latter condense into a state with a characteristic chiral soliton excitation that we assume to coexist with the multiferroic and collinear phases. Close to H_c , the long-range order of the multiferroic phase is weakened and, at the same time, the short-range modulated collinear phase is not yet fully established. The coexistence of both later phases has been shown from neutron data³⁵, giving further credit to the possible coexistence of a third phase in the same magnetic field range. From the measurements shown in Fig. 3, we can estimate that this state occurs only for magnetic fields ranging from approximately 6.5 to 8.0 T. Here we measure a contribution to the permittivity spectra that, despite being located in the GHz regime, does not show overdamped relaxational but excitational character with comparably low damping. This low-energy excitation with a tiny gap of $E_{\text{SE}} \approx 14.1$ μeV is consistent with the predicted chiral soliton excitation of a quantum spin-liquid state in LiCuVO_4 ⁸. To determine the correlation length and to investigate the possible quantum spin-liquid behavior further neutron scattering experiments would be helpful.

Methods

Single crystals of LiCuVO_4 were grown from LiVO_3 flux in the temperature range between 910 and 853 K with an applied cooling rate of 0.1 K/h.

Dielectric spectroscopy. To observe the fluctuation dynamics at the edge of the multiferroic phase we mounted a LiCuVO_4 crystal on a microstrip sample holder for dielectric spectroscopy measurements in the GHz range. The measurements were done with different network analyzers (Agilent PNA-X and Rohde & Schwarz ZVB4 and ZNB8) in two cryostats, a top-loading dilution refrigerator (Oxford Instruments KELVINOX) and a Quantum Design PPMS.

Thermal expansion. Thermal expansion was measured in a home-built capacitance dilatometer with an ac capacitance bridge (Andeen-Hagerling AH2550). The uniaxial thermal expansion coefficient was obtained numerically via $\alpha_i = 1/L \partial \Delta L / \partial T$. The magnetic Grüneisen parameter Γ_H was measured using a home-built calorimeter with a technique explained in ref. ³².

Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

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Author contributions

P.B. and L.B. grew the samples for all experiments. D.B., S.K., and T.L. planned, performed, and interpreted the measurements of thermal expansion and Grüneisen parameter. C.P.G. and J.H. planned and interpreted the dielectric measurements, C.P.G. performed the measurement and analysis of the dielectric data. The manuscript was prepared by C.P.G., J.H., and T.L. with the support of all authors.

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Competing interests

The authors declare no competing interests.

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