Giant dielectric nonlinearities at a magnetic Bose–Einstein condensation

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We experimentally investigate the dielectric response of the low-dimensional gapped quantum magnet Cu$_2$Cl$_4$H$_8$C$_4$SO$_2$ near a magnetic field-induced quantum critical point, which separates the quantum-disordered and helimagnetic ground states. Contrary to previous speculations, we find the dielectric susceptibility to be non-critical. The transition is purely magnetic and is perhaps one of the best known realizations of Bose–Einstein condensation of magnons. The material is thus an improper quantum ferroelectric. Despite that, we find that the magnetocapacitive effect associated with the transition exhibits huge and very unusual anharmonicities. This behavior is attributed to the motion of chiral domains that seems to persist down to mK temperatures.

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Phase transitions are typically driven by thermal fluctuations. The exception are transitions at $T = 0$, which are driven solely by quantum fluctuations. Any details of the microscopic Hamiltonian become irrelevant at the quantum critical point (QCP), which leads to an astounding universality of finite-temperature behavior [1]. Magnetic insulators, having short-ranged interactions and tunable Hamiltonians, have long served as prototypes for studying such quantum phase transitions (QPTs) [1, 2]. In real compounds other degrees of freedom, such as lattice and charge, may play an additional important role alongside magnetism. Their influence on thermal phase transitions is well documented [3-7]. In studies of magnetic QPTs, however, these extra degrees of freedom have often disregarded. A recent boom of multiferroic materials yielded novel compounds in which the electric polarization is intrinsically coupled to the exotic magnetic order [8-11]. Here the interplay between lattice, charge and magnetism occurs naturally. A few recent studies looked at rare cases in which multiferroicity occurs at QPTs [12-14], but not much work was done to study the criticality of such transitions. Moreover, the very important case of QCP connecting magnetically ordered and quantum-disordered phases, such as in Bose–Einstein condensation (BEC) of magnons [15-18], remains largely unexplored in the context of multiferroic physics.

On the experimental side, some progress occurred very recently when the multiferroic properties of $S = 1/2$ quasi-1D quantum antiferromagnet Cu$_2$Cl$_4$H$_8$C$_4$SO$_2$ (AKA Sul-Cu$_2$Cl$_4$) [17-21] were brought into focus [22]. This material is very different from a panoply of other gapped spin systems in featuring a high degree of geometric frustration of interactions. The result is a magnetic-field induced QPT from a quantum-disordered to a helimagnetic state. This is where the multiferroic properties emerge, invoked via the “spin-current” or “inverse Dzyaloshinskii–Moriya” (DM) mechanism [23, 24]. The most exciting conclusion of previous studies [22] was the possibility of critical dielectric fluctuations in this material. Together with the apparent unconventional critical properties [19, 20] this indicated some novel magnetoelectric order parameter, and possibly a new universality class for the transition. In the present Letter we show that this is not the case, and that electric polarization in Sul-Cu$_2$Cl$_4$ is not a critical quantity. In fact, the QCP is fully consistent with 3D BEC of magnons, and is arguably the “cleanest” realization of such among all known materials. While electric polarization plays a dependent role, it is by no means irrelevant. On the contrary, near the magnetic QCP in Sul-Cu$_2$Cl$_4$ we find spectacular anomalies in the non-linear dielectric response.

Sul-Cu$_2$Cl$_4$ belongs to a rapidly growing family of insulating metalorganic Heisenberg spin systems [25]. Its magnetic properties are due to $S = 1/2$ Cu$^{2+}$ ions. The spins are antiferromagnetically coupled into one-dimensional structures, which can be described as highly frustrated 4-leg spin tubes, running along the $c$ axis of the triclinic structure (see Refs. [19, 20] for more details). This layout with an even number of “legs” is responsible for the non-magnetic quantum-disordered ground state, and a gap $\Delta \approx 0.52$ meV in the spin excitation spectrum [19]. Due to a geometric frustration of exchange interactions, the dispersion minimum for the triplet of lowest-energy $S = 1$ excitations occurs at an incommensurate wave vector. As the result, in an external magnetic field $H_c = \Delta/g\mu_B \approx 3.7$ T for $H \parallel b$, Sul-Cu$_2$Cl$_4$ undergoes a soft-mode ordering transition with incommensurate propagation vector $\mathbf{Q} = (-0.22, 0, 0.48)$. The structure of the ordered high-field phase has been resolved by neutron diffraction [20]. The spin components transverse to $\mathbf{H}$ form a spiral such that $\langle S_1 \perp (\mathbf{r}) \rangle = S_1 \cos(\mathbf{Qr}) + S_2 \sin(\mathbf{Qr})$ with $\mathbf{S}_1 \parallel S_2$. This spiral arrangement lacks an inversion symmetry and hence induces an electric polarization $\mathbf{P} \propto [\mathbf{S}_1 \times \mathbf{S}_2] \times \mathbf{Q}$ [23, 24]. To date, this polarization has not been directly measured, and is likely to be extremely small. Instead, previous studies of Schrettle et al. [22] probed the corresponding dielectric permittivity $\varepsilon$. The apparent divergence of this quantity at the phase transition was taken as a sign of $\mathbf{P}$ going criti-
The prominent capacitance peak seen at high temperatures is what Ref. [22] must have taken for a divergent $\varepsilon$. In fact, at low temperatures, as the QCP is approached, the anomaly weakens, and transforms into a small and rounded step at $T \rightarrow 0$. The peak amplitude of $\Delta C$ decreases with the temperature almost linearly. Moreover, as can be seen in the low-temperature constant-$H$ scans in Fig. 1b, outside of the ordered phase there is no detectable change in the dielectric constant even along the critical trajectory $H = H_c = 3.43 \pm 0.01$ T [27]. Clearly, $\varepsilon$ is not a critical susceptibility of the phase transition in Sulfur-Cu$_2$Cl$_4$. Instead, the observed behavior is consistent with the dielectric anomaly being proportional to the anomaly in specific heat [28]. This is typical for an improper ferroelectric with quadratic-linear coupling between the ordering (magnetic) and non-ordering (polarization) parameters [7]. Exactly this type of coupling is expected in the inverse DM scenario [24]. We conclude that the QCP in Sulfur-Cu$_2$Cl$_4$ is a purely magnetic one. The anomalous contribution to dielectric susceptibility is confined to ordered phase being triggered by the spontaneous magnetic order. The situation is akin to conventional thermal phase transitions in improper ferroelectrics [4-5, 29].

Although ferroelectricity does not drive the QPT in Sulfur-Cu$_2$Cl$_4$, the very precise measurements of $\varepsilon$ enable us
to extract the critical field with an unprecedented accuracy for this compound, and thereby elucidate the nature of the magnetic transition. At any given temperature, associating the transition with a maximum of slope in $\varepsilon (H)$ yields the phase diagram shown in Fig. 2. The parameter most relevant to the QCP is the so-called crossover exponent $\varphi$, which defines the phase boundary at $T \to 0$:

$$H - H_c \propto T^{1/\varphi}.$$  

(1)

A shrinking fit window analysis [30] of our data reveals that a true power-law behavior extends only up to $T \sim 300$ mK. This range is barely accessible to specific heat studies [28]. However, as can be seen from the Fig. 2 inset, our dielectric data are dense and accurate enough to yield a very reliable estimate $\varphi = 0.63 \pm 0.03$ for that fitting range [31]. The anomalous result $\varphi \approx 0.34$ previously obtained by neutron scattering [20] is likely due to insufficient number of data points and dimensional crossover effects that affect the determination of $H_c$ from magnetic Bragg intensity measurements. Our present result $\varphi \approx 0.63$ is fully consistent with $\varphi = 2/3$ expected for a BEC of magnons transition [15, 16, 32, 33].

This finding is significant. Indeed, despite numerous claims to the contrary, the field-induced transition in most gapped quantum magnets is, strictly speaking, not in the BEC universality class. Instead, due to magnetic anisotropy which breaks the prerequisite $SO(2)$ symmetry of the Hamiltonian in materials like TiCuCl$_3$ [34, 35] and IPA-CuCl$_3$ [36], it is actually of the Ising type [37] with an energy gap in the magnetically ordered state [38–40]. Even in the one known tetragonal compound DTN [41, 42] the transition is likely discontinuous due to magnetoelastic coupling and a spontaneous lattice distortion [37], showing critical exponents inconsistent with BEC [43]. In contrast to all these commensurately ordering materials, the $SO(2) \equiv U(1)$ symmetry in Sul-Cu$_2$Cl$_4$ is protected by its incommensurability. Indeed, the phase of the incommensurate spiral structure is decoupled from any magnetic anisotropy terms that are commensurate, and the ordered state necessarily has a gapless “sliding mode” [45].

Even though in Sul-Cu$_2$Cl$_4$ the dielectric properties don’t affect the QCP, the reverse most certainly does occur. A careful examination of the observed magnetocapacitive effect reveals its amazingly nonlinear nature. Just varying the probing voltage leads to a drastic change of the amplitude of the dielectric anomaly, without affecting the onset of the transition or the background $C_0$. An example of such dependence is shown in Fig. 1: The peak magnitude $\Delta C_{\text{max}}$ at a fixed temperature monotonously decreases with the decrease of the voltage. It is not even clear if it can be extrapolated to a “true” non-zero value in the zero-voltage limit. Note that the electrical fields producing this non-linearity are very modest (upper scale in Fig. 1).

FIG. 3. (Color online) Phase transition in Sul-Cu$_2$Cl$_4$ as seen by nonlinear dielectric spectroscopy. Current harmonics $I_n (H)$ ($n$ from 2 to 6) induced by an applied sine voltage are plotted as a functions of magnetic field at $T = 100$ mK. Projections of $I_n (H)$ onto Re-$H$, Im-$H$ and Re-Im planes are also shown. Drive voltage has amplitude $V = 30$ V and frequency $\omega/2\pi = 551$ Hz.

The best indicator of nonlinear behavior are higher-order harmonics in AC measurements. In our case of Sul-Cu$_2$Cl$_4$, we tracked the complex harmonics of the displacement current, induced by the applied AC voltage, making use of the SR7270 lock-in amplifier. A representative data set (note the low $T = 100$ mK) is shown in Fig. 3. Below the critical field the nonlinear response is zero. However, inside the ordered helimagnetic phase all current harmonics with frequencies up to $6 \omega$ go on a wild ride in the complex plane as a function of applied magnetic field. At still higher fields, they gradually decrease and are eventually suppressed, as is the linear magnetocapacitive effect. Since the displacement charge flow is related to the change of sample polarization $\partial P/\partial t$, the appearance of current harmonics under a periodic voltage $V \sin(\omega t)$ is the direct consequence of the polarization nonlinearity:

$$P(E) = P_0 + \varepsilon_0 \left( \chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \ldots \right).$$  

(2)

In this expansion $\chi_1 = \varepsilon - 1$ is the conventional first-order susceptibility, while $\chi_n = \frac{1}{2n!} \frac{\partial^n P}{\partial E^n}$ are the nonlinear hypersusceptibilities [46, 48]. The presence of even current harmonics manifests the presence of even powers of $E$ in the expansion (2). This implies $P(-E) \neq -P(E)$ and provides an indirect evidence of non-zero sponta-
FIG. 4. (Color online) Nonlinear contributions to the magnetocapacitive effect in Sul-Cu\textsubscript{2}Cl\textsubscript{4} at $T=100$ mK $C_n$ (see text) as a functions of magnetic field. Thick dashed red and dotted blue lines are real and imaginary parts of $C_n$ and thin black line is the absolute value. Vertical line marks the phase transition field.

How strong are the observed non-linearities? The exact value of $P_0$ can not be derived from the data in Fig. 3 but the magnitudes of the nonlinear terms can. The algebra required to restore the hypersusceptibilities $\chi_n$ from current harmonics $I_n$ is summarized in Ref. [49]. To allow a quantitative comparison between different hypersusceptibilities (which are of different physical dimension), we present them in the form of anharmonic capacitance contributions $C_n = \varepsilon_0 \chi_n \frac{S}{\alpha} E^{n-1}$ [50]. The resulting $C_n(H)$ for the representative $T=100$ mK case are plotted in Fig. 4. By comparing this plot to Fig. 1 one can immediately see that some of anharmonic contributions have the same order of magnitude, as the linear magnetocapacitance term. Already at a very moderate electric field $E \sim 0.3$ kV/cm the nonlinear response is at least as important as the linear one. Such a giant dielectric nonlinearity at quantum phase transition of non-electric nature is a new and unexpected phenomenon.

A nonlinear electric response and hypersusceptibilities were studied in proper ferroelectrics [51, 52], relaxors [53] and glasses [54, 55]. Unfortunately, none of the above are directly the present case. Our present understanding is that the anharmonicity roots in the motion of helimagnetic domains of opposite chirality, which appear immediately above the transition field. An unusual circumstance is that domains seem to remain mobile even in absence of the thermal fluctuations, in zero-temperature limit, which suggests an exotic pinning mechanism. Since even tiny amounts of impurities are known to have a huge effect on the phase transition in Sul-Cu\textsubscript{2}Cl\textsubscript{4}, in the future it will be very interesting to investigate their influence on the dielectric response and domain mobility.

In summary, the field-induced QCP in Sul-Cu\textsubscript{2}Cl\textsubscript{4} is a purely magnetic one, and appears to be one of the best realizations of magnetic BEC. The material can thus be referred to as “improper quantum ferroelectric”. Its unusual dielectric response is confined to the magnetically ordered phase, but is hugely non-linear even in very modest drive fields.

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A co-aligned mosaic of \( d \sim 0.5 \) mm-thin single crystals of Sul-Cu\(_2\)Cl\(_4\) was sandwiched between the copper plates of a capacitor, that were parallel to the crystallographic (ac) plane. The magnetic field \( \mathbf{H} \) was applied parallel to the a axis. It defines the spiral plane, the expected polarization being along \( \mathbf{b}^* \parallel \mathbf{E} \). Special care was taken to prevent any exposure of the sample to the atmosphere to avoid deterioration. Measurements were done using an AH2550A capacitance bridge. The capacitor plate area was \( A = 8 \times 8 \) mm\(^2\). Due to the difficulty of precisely measuring the filling factor of the Sul-Cu\(_2\)Cl\(_4\) “effective capacitor”, we prefer to report the results as a change in sample capacitance \( C = \frac{1}{2} \varepsilon \varepsilon_0 \) rather than a change in dielectric constant. The values of \( \varepsilon \) mentioned in the text should be considered as estimates.

The observed critical filed value is different from the one quoted in the introduction, due to the direction of applied field in the present study (\( \mathbf{H} || \mathbf{a} \)) being different from that in previous neutron \([20]\) and calorimetry \([25]\) experiments (\( \mathbf{H} || \mathbf{b} \)).

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For a wider fitting range \( \lesssim 1 \) K, we get \( \varphi \approx 0.5 \), thus recovering the value previously found by specific heat measurements \([18, 28]\).

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