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Cite as: AIP Advances 9, 125329 (2019); https://doi.org/10.1063/1.5130403
Submitted: 04 October 2019 . Accepted: 20 November 2019 . Published Online: 26 December 2019

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ABSTRACT

We present magnetic field-dependent specific heat (C) data for [Cu(pyO)₄(NO₃)₂] (pyO = pyridine oxide) (CPN), a molecular salt shown to be quasi-1D, and for a quasi-2D analogue, [Cu(pyO)₆]₂(BF₄)₂ (CPB). For CPN, a sharp feature indicating 3D ordering is observed at 0.16K in zero-field. As the field, H, is increased, the ordering temperature first increases, as expected for quasi-1D antiferromagnets, before decreasing rapidly for H above 3T. The field also transfers the entropy of short-range ordering (SRO) in the spin chains into the 3D ordering peak. At our lowest accessible temperature, T ∼ 0.096K, C/T exhibits an enhanced peak at the critical field. Qualitatively similar behavior is found in CPB. These results demonstrate a potentially powerful new materials route to study quantum phase transitions.

The search for new quantum magnets is motivated by the desire to create a coherent quantum spin liquid (QSL), and to control excitations out of this state for potential quantum information applications. Much work has focused on s = 1/2 spin-containing compounds, particularly on frustrating 2D lattices where classical long range order (LRO) is suppressed, such as in the κ-ET salt and Herbertsmithite, with triangular and kagome lattices respectively. Other realizations are found in 1D lattices exhibiting Luttinger liquid (LL) behavior or a transition to a Bose Einstein Condensate (BEC) of triplons. The LL systems are spin-½ chains with such weak inter-chain exchange interaction that the transition to LRO occurs at temperatures well below the in-chain exchange energy but exhibit a large Sommerfeld specific heat coefficient above this temperature. The BEC systems such as TiCuCl₃ or BaCuSi₂O₆ exhibit a spin-dimer singlet state at low field and at higher field, level crossing which enables the triplet levels to undergo LRO at a quantum critical point (QCP), a phenomenon known as triplon condensation. All of these systems possess characteristics that seem to compromise the realization of quantum magnetism. For example, the frustrated 2D systems mentioned above possess defect levels that obscure a clean QSL interpretation, and the triplon condensation occurs at magnetic fields high enough to restrict many types of measurements.

Recently we explored a different route towards creating highly fluctuating quantum magnetism. We showed that the quasi-1D, s = 1/2, Heisenberg antiferromagnet (AF), K₂PbCu(NO₃)₆, (Cu-Elpasolite) exhibits a large peak in the specific heat, C, at its QCP. Such a large entropy release is not seen in 3D AFs and the size of the peak is suggestive of a spinon origin, which would imply that the system reverts to 1D behavior at the QCP. Considering the entire phase diagram for K₂PbCu(NO₃)₆, the entropy release at the QCP can be associated with the field-induced downshift of the AF short range order (SRO) peak in C. This peak eventually merges with the AF phase boundary at the QCP, thus leading to a large peak in C at this point. Regarding a theoretical explanation, although the magneto-thermodynamics of linear chain systems has been addressed in the low-field limit, the behavior over the whole field and temperature range, including both quantum critical and SRO regions, has yet to be addressed. Of particular interest are two questions: 1) is SRO-LRO merging seen in other quasi-1D systems and; 2) is SRO-LRO merging evident in quasi-2D systems? If the phenomenon observed in Cu-Elpasolite is generic to low-D magnets,
then it may represent a powerful way to realize quantum criticality and coherence.

In the present work, we explore two different systems to test the generality of the picture of SRO-LRO merging. We study the \( s = 1/2 \) chain system, [Cu(pyO)\(_6\)](NO\(_3\))\(_2\) (pyO = pyridine oxide) (CPN), who quasi-1D interactions arise from a high-temperature Jahn-Teller (JT) distortion of the Cu\(^{2+}\) octahedron \(^9\) that leads to shorter superexchange pathways in one direction. Long range order for \( H = 0 \) is evidenced by a sharp peak in \( C(T) \) at 0.16 K. We also explore the quasi-2D system, [Cu(pyO)\(_6\)](BF\(_4\))\(_2\) (CPB). As in CPN, low-dimensionality in CPB results from a JT distortion of the CuO\(_6\) octahedra, but here the presence of the BF\(_4\) anion leads to uniformly elongated Cu-O bonds, thus creating planes of Cu\(^{2+}\) ions and 2D instead of 1D behavior. At zero field, CPB exhibits a small 3D-LRO peak at 0.65 K, preceded by a broad 2D-SRO peak at 1 K. These compounds are members of a large family of isostructural pyridine N-oxide systems, \(^9\) the magnetic sites of which can be populated with any of the late 3d metals, but which have been studied mainly for \( H = 0 \).

The samples were synthesized by the previously reported method.\(^1\) Powder X-ray diffraction was used to confirm the trigonal phase of each compound. Magnetic susceptibility, \( \chi(T) \), was measured on single crystals using a Quantum Design MPMS dc-magnetometer. Specific heat measurements were performed using the semi-adiabatic technique. Initial measurements were attempted on a single crystal of CPN but the internal relaxation time below 1K became large enough to prohibit this approach. Therefore, we used powdered samples and cold-sintered them at 2 kbar with fine-grained Ag powder to facilitate thermal equilibration. The Ag contribution was measured separately and subtracted from the data. The agreement of our \( H = 0 \) data with previously published work on CPB\(^7\) provides assurance that the sintering pressure did not affect the exchange constants. The samples were mounted on a sapphire calorimeter which was inserted into a top-loading \(^3\)He-\(^4\)He dilution refrigerator.

Both CPN and CPB possess the trigonal \( R\bar{3} \) space group structure at high temperature, with JT transitions between 30-60 K to triclinic arrangements that dictate the collective magnetism at lower temperatures.\(^1\) The magnetic lattice of \( s = 1/2 \) Cu\(^{2+}\) ions in these systems has been discussed previously.\(^6\) For both compounds, the superexchange path is Cu-O-O-Cu where the oxygen ions belong to the pyO molecules. For CPB, the JT effect results in a ferrodistortive elongation of the CuO\(_6\) octahedra along the primitive cell axis, creating a 2D quadratic layer Heisenberg AF.\(^4\) For compounds such as [Cu(pyO)\(_6\)](ClO\(_4\))\(_2\) (CPC) the deviation from a cubic environment is antiferrodistortive in the \( a\)-\( b \) plane thus leading to dominant 1D superexchange paths in the \( c \)-direction.\(^1\) Below we argue that this latter type of distortion also occurs in CPN leading to quasi-1D magnetism. Data of \( \chi(T) \) for both CPB and CPN are shown in the inset of Fig. 1 and for temperatures between 20 and 200 K, yield effective moments of \( \mu_{\text{eff}} = 1.84 \) and 1.88 \( \mu_B \) respectively, consistent with expectations for \( s = 1/2 \) and \( g = 2.13 \sim 2.17 \). Values of \( g \) in this range are not unexpected for 3d\(^{10}\) ions in a distorted ligand environment even in the dilute case.\(^4\) We expect that such small anisotropy may be determinative for selecting the 3D ordering direction for the spins, but otherwise unimportant for the physics discussed here.

The quasi-2D nature of CPB has been modeled previously by a square lattice Heisenberg AF with an in-plane exchange energy of \( J/\kappa_B = 1.1 \pm 0.05 \) K, determined by fitting the specific heat SRO peak to the Padé approximants to the high temperature series expansion for this model.\(^12\) The behavior seen in CPN is similar to that found in CPC, whose low-temperature magnetism is well modeled by the Bonner-Fisher computations for 1D AF Heisenberg chains.\(^13\) In Fig. 1 we show \( C(T) \) for CPN, which displays an SRO peak with maximum at 1.40K and a sharp LRO anomaly at \( T_N = 0.16K \), similar in magnitude to CPC’s LRO anomaly at 0.14K.\(^12\) In order to compare with the Bonner-Fisher theory, a lattice contribution must be subtracted from the CPN data. Given the lack of a non-magnetic isomorph, and given the large uncertainty introduced by the addendum and silver contributions to the total heat capacity, we restricted the range of comparison to \( T < 3K \), and identified a \( T^2 \) contribution to fit the high-temperature tail of the Bonner-Fisher \( C(T) \). After subtracting this lattice contribution, we find good agreement between the main peak in \( C(T) \) and the Bonner-Fisher result for a Heisenberg AF infinite chain,\(^12\) also shown in Fig. 1. The good agreement between our data and the model supports that CPN is a quasi-1D Heisenberg AF system that undergoes 3D LRO at 0.16K.

In Fig. 2, \( C(T)/T \) data are shown for CPN in a field. With increasing \( H \) up to 3T, the LRO peak increases in magnitude and shifts to higher \( T \), a reflection of spin dimensionality crossover from Heisenberg to XY behavior, an effect that is enhanced in low D systems\(^16\) and also seen in Cu-EIpasolite.\(^3\) Increasing \( H \) above \( H = 3 \) T eventually reduces the peak position as it must for AF interactions, but the peak magnitude continues to increase. At the same time, the entropy in the SRO peak, clearly present at 1K in zero field, shifts downward in temperature, merging with the LRO peak. This effect of the SRO and LRO entropies merging was also observed in Cu-EIpsolite.\(^3\) We augmented the temperature scans with scans of \( C \) as a function of \( H \) at constant \( T \), shown in the inset of Fig. 2, and we
FIG. 2. Specific heat divided by temperature versus temperature for \([\text{Cu(pyO)}_6\text{(NO}_3\text{)}_2\) at four different field values. Inset: Specific heat divided by temperature versus field at two different temperatures.

Note the magnitude of the \(C(H)/T\) peak, which reaches 8 J/moleK at 0.092K. The much larger size of this peak as compared to that found at 1.60K in Cu-Elpasolite can be understood partially within the spinon framework proposed in that work. From the ratio of the SRO peak positions (1.74), we infer an intra-chain exchange constant of \(J/k_B = 3.1\) K for CPN. The Zeeman energy at the \(C(H)\) peak of 4.6T, corresponding to the lowest measured temperature, is 6.2\(k_B\), hence \(g\mu_BH/J\ = 2.0\), which is extremely close to the critical field for isolated chains. If the \(C(H)\) peak is indeed related to the spinon contribution of an isolated chain then this implies that the spinon velocity is very small, which can help to explain the large magnitude of the \(C(H)\) peak that we observe for CPN. Higher precision work will require additional measurements at temperatures less than 0.096K in order to model the nuclear contributions from both CPN and Ag powder. These measurements will present a technical challenge since, even with Ag powder sintering, the internal relaxation times in our samples became prohibitively large around 0.1K.

In Fig. 3 are shown \(C(T)/T\) data for CPB for different field values. For \(H = 0\), one sees the broad SRO peak centered at 1.02K, followed by a sharp LRO anomaly at 0.65K, consistent with previous work. On increasing \(H\), similar to the 1D cases discussed above, \(T_N\) also increases for \(H < 4T\), which can be understood as an intermediate case between the calculations of symmetry crossover for 1D\(^{16}\) and 3D\(^{15}\) systems. The most striking aspect of these data, however, is the observation that between \(H = 0\) and 4T, the amount of entropy in the LRO peak grows by at least an order of magnitude, a conservative estimate that recognizes the difficulty in separating the divergent contribution from the SRO peak for \(H = 0\). At the lowest temperatures we also performed \(H\)-scans shown in the inset of Fig. 3. Here, as for CPN, a peak occurs in \(C(H)\) that greatly exceeds the spinon contribution observed for Cu-Elpasolite, but we also see clear evidence for a nuclear contribution in the rise of \(C/T\) on cooling below 0.5K for the \(H = 4, 5,\) and 6 T data sets. As mentioned above, further work to disentangle the nuclear and electronic contributions to \(C/T\) will require additional measurements with enhanced thermal conduction to allow taking lower temperature data. The main result is, however, the SRO-LRO merging, which was previously seen only in the 1D systems discussed above. By analogy to these systems, we might be seeing in CPB precursors of the phenomenon where the physics of the low-dimensional sublattice re-appears at the QCP. If true, then studying such systems at the QCP constitutes a

FIG. 3. Specific heat divided by temperature versus temperature for \([\text{Cu(pyO)}_6\text{)(BF}_4\text{)}_2\) at five different field values. Inset: Specific heat divided by temperature versus field at three different temperatures.

FIG. 4. Phase boundary for CPN and CPB in reduced units of temperature and field. The lines are a guide to the eye. The phase boundary for a 3D antiferromagnet, Yb\(_2\)Pt\(_4\), is also shown for comparison.
powerful protocol for realizing highly fluctuating quantum magnetism in a 2D system. Moreover, unlike some of the purported QSL candidate materials, one can characterize the effect of disorder on the classical 3D ordering for $H = 0$, and quantify its role de-cohering the quantum state at the critical field.

In Fig. 4, we present the phase boundaries for CPN and CPB, along with the boundary for Yb$_3$Pt$_4$, a canonical 3D AF$^+$ on a reduced $H$, $T$ plot, where $H_c$ is determined from $C(H)$ peak at the lowest attainable temperature. The initial increase of $T_N$ for small fields that is so prominent for CPN and CPB should also be present for Yb$_3$Pt$_4$, but other studies of 3D antiferromagnets have shown the maximum $T_N$ rise to be of order 0.2%, as compared to the 50% and 15% increases seen for CPN and CPB respectively, and therefore not visible from the available data. Further theoretical work to model symmetry crossover in quasi-2D systems is needed to complete the phase diagram comparison.

In summary, we have measured $C(T, H)$ of CPN for both zero and finite fields and find a transition to LRO at 0.16K. We find qualitative agreement with the SRO and LRO features described in previous work on the quasi-1D AFH system Cu-Elpasolite, in particular large peaks in $C(H)$ indicative of significant quantum character close to the QCP. In the quasi-2D AFH system CPB, we measured $C(T, H)$, confirming the existing $H = 0$ data and mapping out the $H$-$T$ phase diagram. Large peaks in $C(H)$ are also observed and interpreted as the merging of SRO and LRO similar to that seen in the quasi-1D systems CPN and Cu-Elpasolite. Further experimental work is needed to assign accurate values to the electronic contributions to $C(T, H)$. Theoretical work is also needed to understand the behavior of quasi-2D magnets in large magnetic fields, en route to highly fluctuating quantum matter at the QCP.

The magneto-thermal measurements were done at UCSC and supported by the U.S. Department of Energy grant DE-SC0017862.

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