Superconducting-like Phase Transition in an Insulating $S = \frac{1}{2}$ 1-D Chain

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Spin $\frac{1}{2}$ 1D chains are ideal for realizations of quantum spin liquids (QSLs). Here we report the discovery of a QSL in Cs$_4$CuSb$_2$Cl$_{12}$. Compared to previously reported $S = \frac{1}{2}$ 1D chains, it possesses a wider temperature range over which the QSL state is stabilized. We find Fermionic-like excitations extending from $T = 0.8$ K up to at least $T = 5$ K, with a large $T$-linear contribution to the specific heat, $\gamma = 31.5(2)$ mJ mol$^{-1}$ K$^{-2}$. At $T = 0.7$ K, there is a second-order phase transition, reminiscent of a superconducting transition, with a specific heat jump of $\Delta C / (\gamma T_J) = 0.8(1)$, that is unchanged by a $\mu_B H = 5$ T magnetic field. Thus Cs$_4$CuSb$_2$Cl$_{12}$ reveals new phenomenology deep in the 1D QSL regime.

Low-dimensional quantum magnets, in which competing exchange interactions govern the magnetic degrees of freedom giving rise to a strong frustration accompanied by enhanced quantum fluctuations, drive novel states of matter such as quantum spin liquids (QSLs). There are a variety of such QSLs hypothesized to exist with different lattice symmetry (2D: triangular, kagomé, honeycomb, 3D: pyrochlore, diamond, hyperkagomé) and various types of magnetic exchange (Heisenberg, Kitaev, Dzyaloshinskii–Moriya). Quantum S = $\frac{1}{2}$ Heisenberg antiferromagnetic 1D chains (HAFCs) are ideal for the realization of QSLs as theoretical analysis with exact solutions are known. The first S = $\frac{1}{2}$ HAFC was realized in CuGeO$_3$. This material undergoes a magnetic phase transition to a long-range ordered state at $T = 14$ K with ~100% entropy recovered. Another seminal example of a S = $\frac{1}{2}$ HAFC is Sr$_2$CuO$_3$. This system exhibits very strong exchange coupling $J/K_b$ with a magnetic phase transition at $T = 20$ K. Such magnetic phase transitions to long-range ordered states prevent realizations of QSLs at the lowest temperature, thereby limiting access to extending QSL phase space.

In this Letter, we report the discovery of a QSL S = $\frac{1}{2}$ HAFC in the new material Cs$_4$CuSb$_2$Cl$_{12}$. It features a wider temperature window over which the QSL state is stabilized. We observe Fermionic-like excitations extending from $T = 0.8$ K up to at least $T = 5$ K, with a large $\gamma = 31.5(2)$ mJ mol$^{-1}$ K$^{-2}$ contribution to the specific heat. At $T_c = 0.7$ K, there is a second-order phase transition, reminiscent of a superconducting transition. An equal entropy contribution gives a specific heat rise of $\Delta C / (\gamma T) = 0.8(1)$, 60% of the weak coupling BCS theory value. In contrast to a superconductor, the transition is unchanged by a $\mu_B H = 1$ T field. The entropy recovered is 0.03(1)% of that expected for S = $\frac{1}{2}$ system (Rln(2)). To our knowledge, this is the first time such a transition has been observed in a HAFC, and indicates that the transition is associated with the Fermionic degrees of freedom in the material.

The structure of Cs$_4$CuSb$_2$Cl$_{12}$ consists of S=1/2 CuCl$_4$ plaquettes connected by 1D chains, Fig. 1. The magnetic susceptibility, measured at $\mu_B H = 5$ T and estimated as $\chi = M/H$, shows a broad maximum around $T = 210$ K, followed by an upturn below $T = 50$ K. This

![Figure 1](image-url)

**Figure 1.** (A) The magnetic susceptibility of Cs$_4$CuSb$_2$Cl$_{12}$ as a function of temperature. A S = $\frac{1}{2}$ HAFC model gives an intrachain exchange coupling of $J/K_b = 186(2)$ K; Inset: single crystal and overall crystal structure; (B) The structure of the 1D chains of Cs$_4$CuSb$_2$Cl$_{12}$, showing the super-exchange interactions along the b-axis.
behavior is characteristic of $S = \frac{1}{2}$ HAFCs in the presence of a few magnetic impurity spins.\textsuperscript{15, 18, 21, 26-27} No indication of a transition to long-range-ordered magnetic state is observed. Quantitative analysis was performed by using the $S = \frac{1}{2}$ HAFC Bonner-Fisher model plus a Curie-Weiss term for the defect spins.\textsuperscript{17, 28-30}

\[
\chi = \frac{1}{C} \frac{1}{T - \theta} + \frac{1}{N} \mu_B^2 \]

where $\chi$ is the observed susceptibility, $C$ is the intrachain exchange interaction, $\theta$ is the Curie constant and Weiss temperature for the defect spins, and $T$ is the temperature. The final fit to the data gives $J/k_B = 186(2)$ K, $C = 0.011(1)$ emu mol-f.u.$^{-1}$ Oe$^{-1}$ and $\theta = -37(5)$ K. The chain interaction strength is consistent with the location of the maximum in the susceptibility, and also with an alternative fit utilizing a dimer model (not shown). The Curie constant is also reasonable, corresponding to 3% of $S = \frac{1}{2}$ impurity spins. The Weiss temperature indicates a larger interaction strength than would be expected between isolated $S = \frac{1}{2}$ units in free space, but is consistent with them being embedded in a QSL.

To further explore the exchange coupling in this system and check whether it is a $S = \frac{1}{2}$ HAFC realization, we performed density functional theory calculations using the recently developed strongly-constrained and appropriately-normed (SCAN) exchange correlation functional.\textsuperscript{31} We used the Cs$_2$CuSb$_2$Cl$_{12}$ crystal structure determined from neutron powder time-of-flight (TOF) and X-ray diffraction, Table 1.\textsuperscript{12} Results of the calculations are shown in Fig. 2. The magnetic density on Cu clearly reveals $d_{x^2-y^2}$ orbitals are polarized, direct evidence of $3d^9$ Cu$^{2+}$ cation with $S = \frac{1}{2}$. Within the ab-plane, the spin of Cu$^{2+}$ also polarizes the $p_x$ and $p_y$ electrons on the four Cl ligand anions, forming CuCl$_4$ units with AF couplings along the b-axis. We also observed similar spin polarization of oxygen in cuprates.\textsuperscript{33-34} To estimate the strength of the exchange coupling $J$, the total energies of the antiferromagnetic (AFM) and ferromagnetic (FM) states of the nearest-neighbor $S = \frac{1}{2}$ Heisenberg Hamiltonian in the mean-field approximation. The difference in total energies of the AFM and FM phases is described in the equation:

\[
\Delta E = E_{\text{AFM}} - E_{\text{FM}} = J N Z \langle S \rangle^2
\]

where $N$ is the total number of magnetic moments, $Z$ is the number of neighboring spins on each site.

Table 1: Crystallographic data for Cs$_2$CuSb$_2$Cl$_{12}$, $\text{C}2/m$, $a = 13.083(3)$ Å, $b = 7.3507(2)$ Å, $c = 13.070(3)$ Å, $\beta = 112.17(3)^{\circ}$.

|     |     |     |     |     |
|-----|-----|-----|-----|-----|
| x   | y   | z   | s.o.f | Uiso |
| Cs1 | 0.1241(2) | 0.0000 | 0.3698(2) | 1 | 0.0229(9) |
| Cs2 | 0.3745(2) | 0.0000 | 0.1299(2) | 1 | 0.0243(9) |
| Sb1 | 0.2520(2) | 0.5000 | 0.2586(2) | 1 | 0.0127(9) |
| Cu1 | 0.0000  | 0.0000 | 0.0000   | 1 | 0.0142(2) |
| Cl1 | 0.1119(5) | 0.2206(8) | 0.1106(5) | 1 | 0.0243(2) |
| Cl2 | 0.3739(6) | 0.5000 | 0.1353(6) | 1 | 0.0238(2) |
| Cl3 | 0.3693(4) | 0.2626(7) | 0.3728(4) | 1 | 0.0239(2) |
| Cl4 | 0.1345(6) | 0.5000 | 0.3769(6) | 1 | 0.0239(2) |

As the spin density supports the predominance of intrachain interactions, $Z = 2$. The calculations were normalized to one formula unit, so $N = 1$. Our first-principles computations for the total energies of the AFM and FM states resulted in $J/k_B \approx 200$ to 800 K (depending on the precise approximations used), which of the same order of magnitude as the $J/k_B$ value of 186(2) K observed experimentally.

Figure 2. (A) Unfolded band structure of Cs$_2$CuSb$_2$Cl$_{12}$ AFM 1-D chain. The unfolding maps the band structure of the 2×2×1 AFM supercell into that of the 1×1×1 non-magnetic primitive cell, and a weaker spectral weight (purple color on the left end of the color bar) represents the band structure is more significantly affected by the magnetism. The inset shows the band path in the primitive cell Brillouin zone. (B) Spin-polarized density of states (DOS). (C) Calculated magnetic density. The red and blue isosurfaces denote the spin up and spin down charge densities, respectively. Cu ions form AFM chains within the xy-plane, but they do not have magnetic coupling across the planes. The open squares (□) denote empty sites.

The calculated magnetic moment is 0.52 $\mu_B$ on Cu, and there is also considerable magnetization on the ligand Cl with a magnetic moment of 0.06 $\mu_B$. The theoretical bandgap is 0.28 eV, which is smaller than the experimental value of ~ 1 eV estimated from the UV-Vis spectroscopy measurements. The valence band maximum is mostly composed of the Cu-$d_{x^2-y^2}$, Cl-p and Sb-s states. The conduction band minimum is isolated from other bands, and mainly derived from Cu $d_{x^2-y^2}$ states with some hybridized Cl-p states.
Thus DFT also supports Cs$_4$CuSb$_2$Cl$_{12}$ as a realization of a 1D HAFC. To elucidate the thermodynamics of the ground state, we performed the heat capacity measurements over the range 2 K ≤ T ≤ 300 K. For T ≥ 2 K, there are no sharp anomalies, indicative of a lack of long-range magnetic ordering or other phase transitions (SI). There is, however, an apparent T-linear contribution that extends up to at least T = 5 K.

To further explore this contribution, expected for a 1D HAFC QSL, we performed specific heat measurements in a Quantum Design PPMS dilution refrigerator from T = 0.2 K to T = 3 K, Fig. 3. The total specific heat was modeled following the equation:

$$C_p / T = \gamma + \beta_3 T^2$$

to extract the electronic (\(\gamma\)) and phononic (\(\beta_3\)) contributions to the specific heat. The final fit yields values of

$$\gamma = 31.5(2) \text{ mJ mol}^{-1} \text{ K}^{-2}, \quad \beta_3 = 7.74(5) \text{ mJ mol}^{-1} \text{ K}^{-4},$$

respectively. The presence of a large T-linear contribution is unusual for an electrical insulator; disorder or glassy behavior can produce such behavior, but usually with a much smaller value of \(\gamma\). Further evidence that the T-linear contribution is intrinsic to the HAFC QSL comes from quantitative analysis: the value of \(\gamma\) for a HAFC QSL is given by:

$$\gamma = 2N_Ak_b^{2}/(3J)$$

where \(N_A\) is Avogadro number, \(k_b\) is the Boltzmann constant, and \(J\) is the intrachain exchange interaction strength. We obtain \(J/k_b = 176(2)\) K, which is in reasonable agreement with the \(J/k_b = 186(2)\) K from the magnetic susceptibility.

This T-linear term is disrupted by a phase transition at \(T_c = 0.7\) K. The \(\lambda\)-like anomaly is characteristic of a second-order phase transition. The concomitant loss of a T-linear contribution is reminiscent of the behavior found in a BCS superconductor. Analysis using an equal-entropy construction gives a specific heat jump of \(\Delta C / (\gamma T_c) = 0.8\). This is about 60% of the BCS value for a superconductor. This transition is not, however, to a superconducting state: application of a \(\mu_0H = 5\) T magnetic field does not suppress or move the transition within the resolution of our measurements. The entropy recovered from the transition is estimated to be \(\Delta S = 2 \text{ mJ mol}^{-1} \text{ K}^{-1}\), approximately 0.03% of S = \(\frac{3}{2}\) spins (Rln2). This is two orders of magnitude smaller than the number of defect spins observed in magnetic susceptibility, and almost four orders of magnitude smaller than would be expected if arising from a transition to bulk magnetic order. Taken together, these results imply the \(\gamma\) term is intrinsic to Cs$_4$CuSb$_2$Cl$_{12}$, not due to disorder or impurity spins, and is suggestive of the spinon density of states, i.e., gapless excitations occur from the QSL state.\(^{16, 23, 37-38}\)

**Table 2: A summary of the exchange interaction \(J/k_b\), transition temperature \(T_c\), and normalized factor \((J/k_b)/T_c\) of Cs$_4$CuSb$_2$Cl$_{12}$ and the other S = \(\frac{3}{2}\) HAFCs.**

| Compound       | \(J/k_b\) (K) | \(T_c\) (K) | \((J/k_b)/T_c\) | Ref. |
|----------------|---------------|-------------|-----------------|-----|
| Cs$_4$CuSb$_2$Cl$_{12}$ | 186           | 0.7         | 370             | This work |
| KCuMoO$_4$(OH)  | 238           | 1.5         | 160             | 21  |
| Sr$_2$CuO$_3$   | 220           | 20          | 110             | 26  |
| Nd$_2$CuO$_4$   | 156           | 1.5         | 104             | 27  |
| Ba$_2$CuGeO$_7$ | 540           | 8.8         | 61              | 39  |
| Sm$_2$CuO$_4$   | 189           | 5.9         | 32              | 27  |
| Ba$_2$Cu$_2$Si$_2$O$_7$ | 280     | 9.2         | 30              | 20  |
| VO$_2$Sb$_4$O$_9$ | 245          | 14          | 18              | 40  |
| TiOCl           | 660           | 67          | 10              | 41  |
| CuGeO$_3$       | 88            | 14          | 6.3             | 18  |
| CuSb$_2$O$_4$   | 48.2          | 8.5         | 5.7             | 42  |
| CuCl$_2$        | 90            | 24          | 3.8             | 43  |
| Cs$_4$CuCl$_4$  | 2.0           | 2.0         | 1.0             | 44  |

In short, Cs$_4$CuSb$_2$Cl$_{12}$ harbors a nearly ideal HAFC QSL state, with a superconducting-like phase transition at \(T = 0.7\) K. An obvious question is: why has this not been observed before given the wealth of known 1D HAFC
materials? It may have been possible because Cs$_4$CuSb$_3$Cl$_{12}$ has an exceptionally large temperature window over which the QSL state is stable, as judged by the ratio of the intrachain interaction strength to the ordering or phase transition temperature, Table 2. KCuGaF$_6$ was also realized as a $S=1/2$ HAFC with $J/k_B=100$ K.\(^{36}\) However, the nuclear Schottky contribution becomes overwhelming at low temperature, hindering study of the physics deep in the QSL phase.\(^{36}\) LiCuSbO$_4$ features complex frustrated 1D chain, which cannot be solely described by the HAFC model.\(^{15}\) Cs$_4$CuSb$_3$Cl$_{12}$ exhibits the largest factor of $(J/k_B)/T_{sp}$ indicative of the wide temperature window over which the QSL is stabilized.

In summary, we have provided the first experimental evidence of a superconducting-like phase transition in the new insulating material Cs$_4$CuSb$_3$Cl$_{12}$. This realization of a QSL in this $S=1/2$ HAFC was described from the results of magnetic susceptibility, specific heat, neutron diffraction and DFT computations. Cs$_4$CuSb$_3$Cl$_{12}$ differs from other quantum HAFC systems for the following elements: (i) the large exchange interaction $J/k_B=186(2)$ K, (ii) a wider temperature window over which the QSL is stabilized, (iii) Fermionic-like excitations extending from 0.8 K $< T < 5$ K with a large $\gamma=31.5(2)$ mJ mol$^{-1}$ K$^{-2}$ contribution and (iv) a second-order phase transition, reminiscent of a superconducting transition with $\Delta C / (\gamma T_x) = 0.8$, that removes the T-linear, Fermionic contribution to the specific heat and is unchanged by a $\mu_B H = 5$ T field. Additional characterizations, including thermal transport, ultrasound and inelastic neutron scattering, are underway to help gain a better understanding of the underlying physics of the ability to stabilize QSL over such wide temperature range in this system.

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Superconducting-like Phase Transition in an Insulating $S = \frac{1}{2}$ 1-D Chain

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Synthesis

Polycrystalline Cs$_4$CuSb$_2$Cl$_{12}$ was synthesized through solid-state reactions at 220 °C for 3 days by combining stoichiometric amounts of CsCl, CuCl$_2$ and SbCl$_3$. Dark purple triangular-shaped crystals of Cs$_4$CuSb$_2$Cl$_{12}$ were grown by hydrothermal techniques. The reaction mixture of 1 g of polycrystalline Cs$_4$CuSb$_2$Cl$_{12}$ and 10 mL of 12 M HCl were placed in a 23-mL Teflon-lined stainless steel autoclave. The autoclave was closed, gradually heated up to at 150 °C, held for 3 days, and then slowly cooled to room temperature at a rate of 6 °C h$^{-1}$.

Laboratory Powder X-ray diffraction

Powder X-ray diffraction (PXRD) data were collected at room temperature using Bruker D8 Focus diffractometer with a LynxEye detector using Cu Kα radiation ($\lambda = 1.5424$ Å). Rietveld refinements on PXRD data were performed using TOPAS 4.2.

Single crystal X-ray diffraction

Single crystal X-ray diffraction (SXRD) data were collected at $T = 213$ K using the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013) on a SuperNova diffractometer equipped with Atlas detector using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å). CrysAlisPro was used to refine the unit cell dimensions and for data reduction. The temperature of the sample was controlled using the internal Oxford Instrument Cryojet. The structure was solved using SHELXS-97 and refined using SHELXL-97. All calculations were performed using SHELXL-97 crystallographic software package.$^1$
Powder neutron diffraction

Powder neutron diffraction data were collected using the time-of-flight high-flux NOMAD at the Spallation Neutron Source, Oak Ridge National Laboratory. Rietveld refinements were performed using GSAS in EXPGUI. The broad maximum feature of the magnetic susceptibility of Cs₄CuSb₂Cl₁₂ at T ~ 200 K (Fig. S1) could indicate that the spins were already paired up at high temperature T > 300 K. In order to unambiguously rule out this possibility, time-of-flight neutron powder diffraction (TOF-NPD) measurements were performed at T = 300 K by NOMAD. The TOF-NPD patterns were simultaneously analyzed by Rietveld refinements in order to determine the presence or absence of magnetic ordering. The data were fit well with the crystal structure of Cs₄CuSb₂Cl₁₂ and no additional Bragg peaks attributed to magnetic ordering of any kind are observed (SI). As a test, a magnetic phase was added to the refinement to assess whether magnetic scattering would be visible. To estimate the sensitivity to magnetic order, we used AFM state. This yielded an upper limit on the magnetic moment of 0.2(5) μₜ per Cu.

Table S1: Crystallographic data from X-ray and Neutron TOF

|                  | Neutron TOF    | X-ray          |
|------------------|----------------|----------------|
| T (K)            | 300            | 293            |
| Space group      | C2/m           | C2/m           |
| a                | 13.089(4)      | 13.083(3)      |
| b                | 7.3511(3)      | 7.3507(2)      |
| c                | 13.077(5)      | 13.070(3)      |
| β                | 112.19(4)      | 112.17(3)      |
| R                | 0.112          | 0.0164         |
| Rw               | 0.129          | 0.0398         |
| Χ² or GOF        | 1.67           | 1.02           |

Figure S1. Time-of-flight neutron powder diffraction (TOF-NPD) refinements of Cs₄CuSb₂Cl₁₂, showing the data are fully described by the crystal structure and no long-range magnetic ordering observed.
Physical property measurements

Physical property characterization was performed using Quantum Design Physical Properties Measurement System (PPMS). Magnetization data were collected using the VSM options at $T = 2 – 300$ K under $\mu_0H = 5$ T and converted to magnetic susceptibility using the approximation $\chi = M / H$. Heat capacity data were collected using the semiadiabatic pulse technique (2% heat rise) for $T = 0.2 – 300$ K.

The heat capacity data above $T = 2$ K are modeled very well with one Einstein mode $(E(\theta_E, T))$, one Debye mode $(D(\theta_D, T))$ and electronic contribution $(\gamma)$ following the equation:

$$C_p / T = E(\theta_E, T)/T + D(\theta_D, T)/T + \gamma$$

The Einstein and Debye temperature can be extracted from the fit to be 61(2) K and 178(7) K, respectively.

![Figure S2. The specific heat $C_p/T$ vs $T$ of Cs$_4$CuSb$_2$Cl$_{12}$ from $T = 2$ K to 300 K](image)

Density functional calculations

Density functional calculations are carried out by using the projector augmented-wave method implemented in the Vienna ab initio simulation package (VASP). The recently developed strongly constrained and appropriately normed (SCAN) density functional is used to treat the exchange-correlation interactions. SCAN functional is able to stabilize the magnetic moment on Cu, while the conventional local density approximation (LDA) and generalized gradient approximation (GGA) fail to do...
so. An energy cutoff of 500 eV is to truncate the plane-wave basis, and a $4 \times 4 \times 4$ K-mesh is used in sampling the Brillouin zone of 76-atom cell. All calculations are done with the experimental crystal structure.

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