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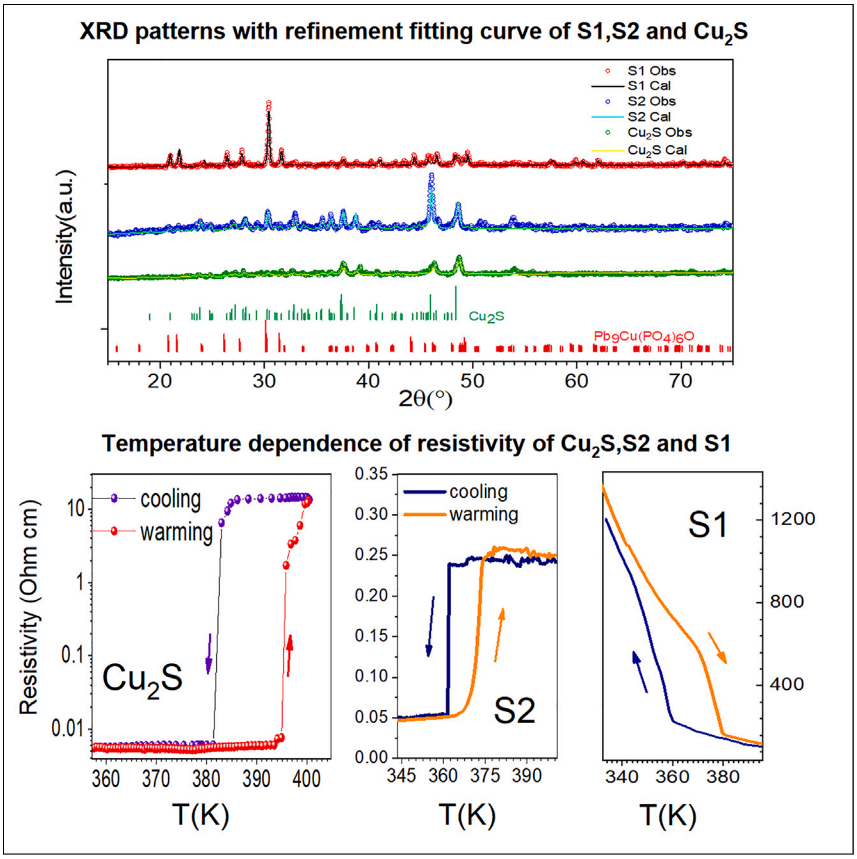
First-order transition in LK-99 containing Cu_2S


XRD patterns with refinement fitting curve of S1,S2 and Cu_2S

Temperature dependence of resistivity of Cu_2S,S2 and S1

The exploration of room temperature superconductors is the central focus of superconducting material research. Sukbae Lee et al. claim that the compound LK-99 ($Pb_{10-x}Cu_x(PO_4)_6O$ [0.9 < x < 1.1]) exhibits room temperature superconductivity under ambient pressure. We measured LK-99 with different contents of Cu_2S and pointed out the so-called superconducting behavior in LK-99 is due to the first-order structural phase transition of Cu_2S at around 400 K.

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Highlights

The superconducting-like behavior in LK-99 is due to Cu_2S

Zero resistance was not observed in LK-99

The magnetic susceptibility behaves as weak diamagnetism in LK-99 containing Cu_2S

2 **Benchmark**
First qualification/assessment of material properties and/or performance

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First-order transition in LK-99 containing Cu_2S

Shilin Zhu,[1,2] Wei Wu,[1,2,*] Zheng Li,[1,2] and Jianlin Luo[1,2,3,*]

SUMMARY

Lee et al. report that the compound LK-99, with a chemical formula of $Pb_{10\text{-}x}Cu_x(PO_4)_6O$ $(0.9 < x < 1.1)$, exhibits room temperature superconductivity under ambient pressure. In this study, we investigated the transport and magnetic properties of pure Cu_2S and LK-99 containing Cu_2S. We observed a sharp superconducting-like transition and a thermal hysteresis behavior in the resistivity and magnetic susceptibility. However, we did not observe zero resistivity below the transition temperature. We argue that the so-called superconducting behavior in LK-99 is most likely due to a reduction in resistivity caused by the first-order structural phase transition of Cu_2S at around 385 K, from the hexagonal structure phase at high temperature to the monoclinic structure phase at low temperature.

INTRODUCTION

Superconductors exhibit zero resistivity and perfect diamagnetism, making them important in applications such as nuclear magnetic resonance, maglev trains, superconducting quantum computing, and lossless power transmission, etc. However, the superconducting transition temperatures of known superconductors at ambient pressure are relatively low. For example, the highest superconducting transition temperature T_c observed in high-temperature cuprates is only around 135 K.[1,2] The hydrogen-rich materials have been discovered under high pressure with T_c approaching room temperature,[3,4] but the extremely high pressure required makes these materials impractical for applications. Therefore, the exploration of room temperature superconductors at ambient pressure is the central focus of superconducting material research and the dream of researchers in the field.

Recently, Lee et al. reported a material called LK-99, a modified-lead apatite crystal structure with the composition $Pb_{10\text{-}x}Cu_x(PO_4)_6O$ $(0.9 < x < 1.1)$ with the hexagonal P63/m structure (space group #176), to be the first room temperature superconductor at ambient pressure.[5–7] They found that LK-99 exhibited a sharp drop in resistance to zero and diamagnetism around 378 K. This report immediately attracted widespread attention, and a number of research groups attempted to verify the superconductivity of LK-99.[8–11] Several groups came up with different conclusions, and none confirmed room temperature superconductivity.

We notice that the reported LK-99 sample contained a certain amount of Cu_2S impurity,[6,9–11] which undergoes a structural phase transition from the hexagonal structure at high temperature to the monoclinic structure at low temperature near 400 K.[12–14] The room temperature structure of Cu_2S is a monoclinic P21/c structure (space group #14). To investigate whether the superconducting-like transition observed is intrinsic for LK-99 or caused by the Cu_2S impurity, we studied the transport and magnetic properties of Cu_2S and the mixture of LK-99 and Cu_2S. We found that the resistivity of Cu_2S decreased by 3–4 orders of magnitude around 385 K,

PROGRESS AND POTENTIAL

LK-99 ($Pb_{10\text{-}x}Cu_x(PO_4)_6O$ $[0.9 < x < 1.1]$) as a potential room temperature superconductor at ambient pressure has garnered significant attention. However, subsequent experiments conducted by various research groups worldwide have failed to observe the distinct resistivity drop of a superconducting-like transition in LK-99. A surge in misleading information about LK-99 calls for urgent clarification of its superconductivity. In this study, we have successfully reproduced the sharp resistivity drop in LK-99. We claim that the reduction in resistivity is a consequence of the first-order structural phase transition of Cu_2S, occurring at approximately 400 K from the hexagonal phase at high temperature to the monoclinic phase at lower temperature. Furthermore, we confirm that LK-99, in its relatively pure form, behaves as a semiconductor rather than a superconductor.

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close to the reported transition temperature and resistance behavior in Lee et al.[5–7] Additionally, we measured the resistivity of the mixture of LK-99 and Cu_2S, which show a sharp resistivity transition at the temperature consistent with the reported findings but without zero resistance. Based on our measurements of resistivity and magnetization, we argue that the superconducting-like behavior in LK-99 most likely originates from the first-order structural phase transition of Cu_2S.

RESULTS AND DISCUSSION

We synthesized two kinds of LK-99 with different Cu_2S content for sample1 (S1) and sample2 (S2), corresponding to different precursors of Lanarkite (L1: annealed in the vacuum) and (L2: annealed in the air), respectively. Then we mixed different precursors of Lanarkite (L1, L2) with Cu_3P powder in the glovebox and sealed into an evacuated quartz tube that annealed in a box muffle furnace. Both Cu_2S and LK-99 phases are observed from the X-ray diffraction (XRD) pattern of the mixtures from S1 and S2. Figures 1A and 1B show the XRD patterns of pure Cu_2S and two mixtures of LK-99 and Cu_2S for S1 and S2. The XRD patterns of Cu_2S phases are well indexed based on a monoclinic-type structure with the space group $P2_1/c$. The LK-99 matches the indexed database, which contains the impurity phase of Cu_2S. From the Rietveld refinement of Figure 1, we obtain the lattice parameters of S1, S2, and Cu_2S, shown in Table 1, and the relative content. The Cu_2S content is approximately 5% in sample 1 (S1) and 70% in sample 2 (S2). Figure 1C shows the main peaks of Cu_2S in pure Cu_2S and S1 and S2 between 45° and 51°. We notice a slight displacement of the peak position for Cu_2S in the mixture compared with pure Cu_2S, which may be attributed to the difference in the S content of Cu_2S.

Figure 2 shows the resistivity of Cu_2S in a temperature range of 2–400 K, plotted on both linear (Figure 2A) and logarithmic scales (Figure 2B), respectively. At around 385 K, a significant decrease in the resistivity of Cu_2S is observed, with a reduction from 13.7 Ohm cm at 385.6 K to 0.006 Ohm cm at 381.5 K, representing a drop of 3–4 orders of magnitude. This drop in resistivity is similar to the resistance drop observed in LK-99, as reported by Lee et al., where the drop temperature is around 378 K.[5–7]

Cu_2S undergoes a structural phase transition from a hexagonal structure at high temperatures to a monoclinic structure at low temperatures near 400 K. This transition has been observed in conductivity and coefficient of thermal expansion measurements.[12],[13] Figure 2B shows the resistivity of Cu_2S maintains a finite non-zero value below the transition temperature, and it gradually increases as the temperature decreases. Additionally, a wide thermal hysteresis of 13.1 K is found in the resistivity of Cu_2S when comparing the cooling curve and warming curve, indicating a first-order phase transition.

Given the sudden drop in resistivity by 3–4 orders of magnitude and the similarities in the near-zero resistance and phase transition temperature with LK-99,[5–7] it strongly suggests that the superconductivity-like behavior in LK-99 reported by Lee et al. is caused by the structural phase transition of the impurity Cu_2S. To verify our hypothesis, we conducted resistivity measurements on the mixture of LK-99 with different contents of Cu_2S, as shown in Figure 3.

Figures 3A and 3B shows a sharp drop in resistivity around 370 K of S2, accompanied by a pronounced thermal hysteresis. As the temperature decreases, the resistivity displays metallic behavior ($d\rho/dT > 0$) over a wide high-temperature range. Below

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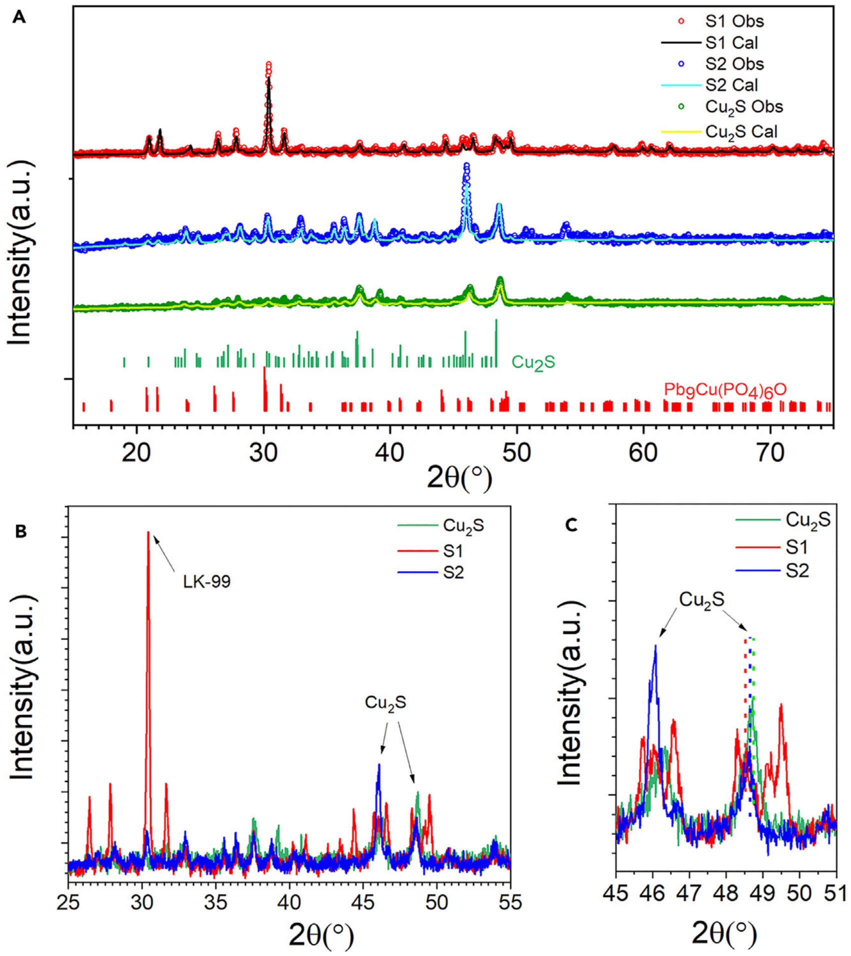

Figure 1. XRD patterns with refinement fitting curve

(A) XRD patterns with refinement fitting curve of pure Cu_2S, S1 and S2.
(B) The main XRD peaks of Cu_2S in pure Cu_2S, S1, and S2.
(C) The enlarged view of XRD in the range between 45° and 51°.

100 K, the resistivity increases with decreasing temperature, showing a semiconducting-like behavior. The sharp drop in resistivity and the transition temperature are similar to that observed by Lee et al.[5–7] Figures 3C and 3D show temperature dependence of the resistivity of S1. We observed a jump in resistivity around 370 K; thermal hysteresis behavior also existed in this sample.

Figure 4A shows the magnetic susceptibility of S2 in a temperature range of 2–400 K, in a field of 1 T. The magnetic susceptibility exhibits diamagnetism with a phase transition occurring at 375 K. Once again, a pounced thermal hysteresis of more than 10 K is observed in the magnetic susceptibility data, suggesting that there is a

Table 1. Lattice parameters of S1, S2, and pure Cu_2S

Sample		a (Å)	b (Å)	c (Å)
S1	LK-99	9.8260 (2)	9.8260 (2)	7.3839 (8)
	Cu_2S	15.2148 (3)	11.890 (1)	13.4855 (8)
S2	LK-99	9.799 (7)	9.799 (7)	7.374 (4)
	Cu_2S	15.2671 (9)	11.8162 (1)	13.4879 (3)
Pure Cu_2S		15.0411 (4)	11.8276 (5)	13.3594 (1)

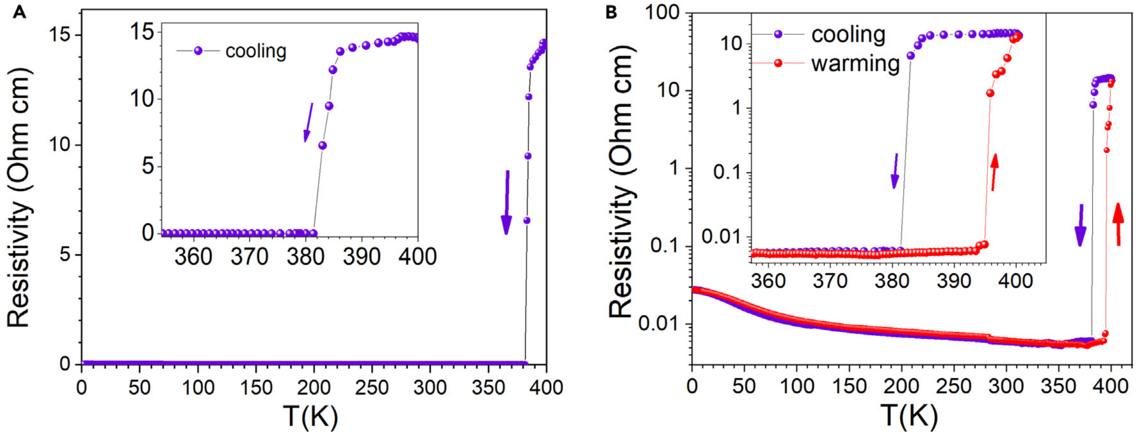

Figure 2. Temperature dependence of resistivity for Cu_2S

(A) Temperature dependence of resistivity of Cu_2S pellet with a very sharp transition.

(B) Temperature dependence of resistivity in cooling and warming course in logarithmic coordinates of Cu_2S with a wide hysteresis behavior.

first-order phase transition. Additionally, the transition temperature range is closely aligned with the structural phase transition temperature of Cu_2S. Figure 4B shows the magnetization as a function of the magnetic field, ranging from −70,000 to 70,000 Oe at various temperatures from 2 to 400 K. It exhibits typical diamagnetic behavior, with no resemblance to the behavior of a superconductor. Furthermore, the magnetism of pure Cu_2S also shows diamagnetism. We notice that a small ferromagnetic component in a large diamagnetic background is observed in LK-99.[15–17] Whether this ferromagnetic component comes from LK-99 itself or impurities in LK-99 deserves further study.

The findings above strongly suggest the superconducting-like transition in LK-99 as reported by Lee et al.[5–7] originates the first-order structural transition of the impurity phase of Cu_2S from a hexagonal structure at high temperature to a monoclinic structure at low temperature around 385 K. It is important to note that this first-order structural transition differs significantly from the second-order superconducting transition. We recommend that Lee et al. perform resistivity measurements during cooling and warming processes on their superconducting-like materials to determine if there is thermal hysteresis.

Conclusion

In conclusion, we measured the transport and magnetic properties of pure Cu_2S as well as the mixture LK-99/Cu_2S and reproduced the experimental results of resistivity. We found a sharp drop in resistivity; however, none of them show zero resistivity. All samples show transitions at around 380 K, which is the phase transition temperature of Cu_2S. The superconducting-like behavior in LK-99 most likely originates from a magnitude reduction in resistivity caused by the first-order structural phase transition of Cu_2S.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Please contact Pro. Jianlin Luo (jlluo@iphy.ac.cn) with any queries.

Materials availability

Cu_2S powder was commercially available (Alfa Aesar) (99.5% −325 mesh). The preparation procedure for LK-99 follows the methodology reported in Lee et al.[5–7] The

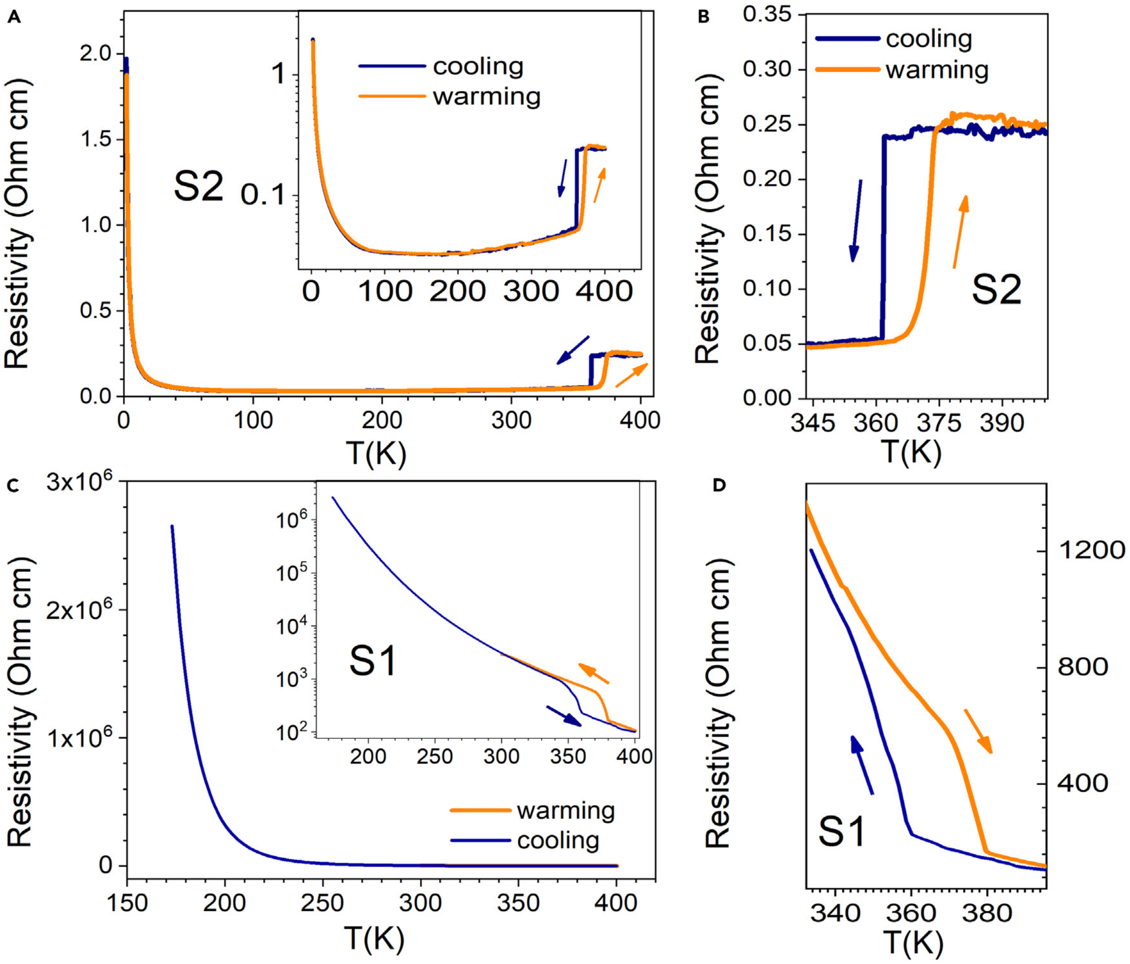

Figure 3. Temperature dependence of resistivity of S2 and S1

(A) Temperature dependence of resistivity of S2. The inset is shown in logarithmic coordinates.

(B) The enlarged view of the transition loop of S2.

(C) Temperature dependence of resistivity of S1. The inset is shown in logarithmic coordinates.

(D) The enlarged view of the transition loop of S1.

precursor Cu_3P and Lanarkite of LK-99 were prepared separately by solid-state reactions. To synthesize Cu_3P, Cu powder (Alfa Aesar 99.99%) was mixed with P (Aladdin 99.999%) in a molar ratio of 3:1 inside a glovebox. The mixture was then pressed into a pellet and sealed in high-vacuum quartz tubes. The tubes were heated to 300°C at a rate of 4°C/min and kept at that temperature for 20 h. Subsequently, the temperature was raised to 900°C for 10 h. Finally, the sample was kept at 900°C for 10 h. Precursor of Lanarkite was obtained by mixing stoichiometric of commercially available $Pb(SO)_4$ powder (Aladdin 99.99%) and PbO powder (Aladdin 99.999%) in a glovebox, and we then annealed the mixture to 725°C at a rate of 4°C/min for 24 h in the vacuum (sealed in the quartz) (L1) and in the air (L2), respectively. (Annealed in the air and in the vacuum will affect Cu_2S content in the final products.) Polycrystalline samples of LK-99 were prepared by solid-state reactions of Cu_3P powder and Lanarkite $Pb_2(SO_4)O$ powder in a 1:1 stoichiometric ratio. The resulting powders were pressed into pellets and sealed into evacuated fused silica ampoules. The ampoules were annealed at 925°C (heating rate: 5°C/min) for 24 h in a box furnace. After cooling to room temperature, the samples were ground in argon atmosphere, pressed into pellets, and then annealed again at 925°C for 24 h.

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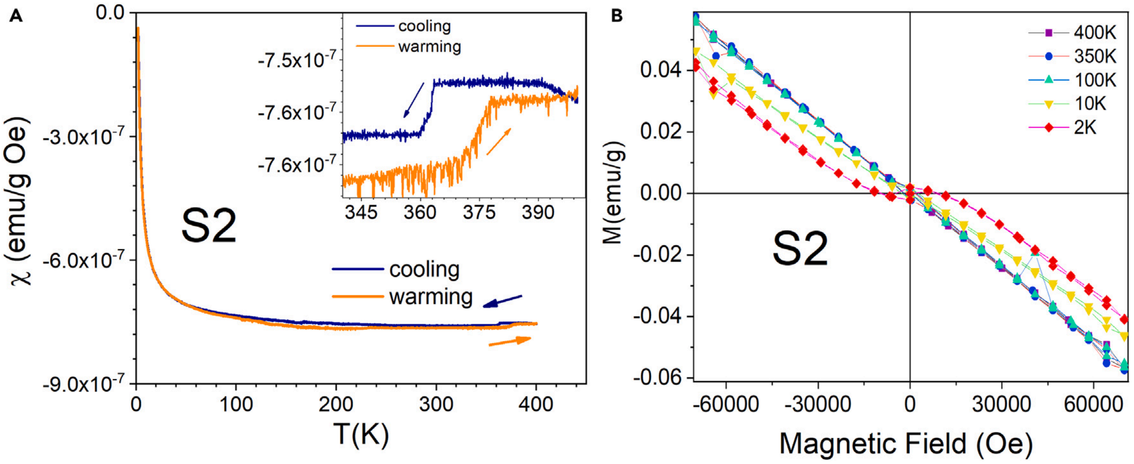

Figure 4. Temperature dependence of diamagnetic susceptibilities and M-H plot for S2

(A) Temperature dependence of diamagnetic susceptibilities measured in S2 at 1 T in cooling and warming course.

(B) The magnetic field dependence of the magnetic moment of S2.

Data and code availability

All data reported in this paper will be shared by the lead contact upon request.

X-ray powder diffraction

All products were structurally characterized using X-ray powder diffraction (Rigaku) in the Bragg-Brentano geometry, equipped with a Cu Ka X-ray source (λ = 1.5406 Å). Rietveld refinements were performed using TOPAS software.

Resistivity and magnetic susceptibility measurements

The resistivity was measured using a standard 4-probe method between 2 and 400 K in the PPMS system of Quantum Design Company. To measure transport properties, Cu_2S powder was loaded into a metallic die and pressed into a dense pellet. The magnetic susceptibility was measured in the temperature range of 2–400 K using a SQUID VSM Magnetometer of Quantum Design Company.

ACKNOWLEDGMENTS

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AUTHOR CONTRIBUTIONS

L.J. conceived the project and designed the experiments. Z.S., L.Z., and W.W. performed the experiments, synthesized the materials, and analyzed the data. All authors participated in the discussion and revision of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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INCLUSION AND DIVERSITY

We support inclusive, diverse, and equitable conduct of research.

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