Bulk superconductivity and Pauli paramagnetism in nearly stoichiometric $CuCo_2S_4$

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It has long remained elusive whether $CuCo_2S_4$ thiospinel shows bulk superconductivity (SC). Here we clarify the issue by studying the samples of sulfur-deficient $CuCo_2S_{3.7}$ and sulfurized $CuCo_2S_4$. The sample $CuCo_2S_{3.7}$ has a smaller lattice constant of $a = 9.454$ Å, and it is not superconducting down to 1.8 K. After a full sulfurization, the a axis of the thiospinel phase increases to 9.475 Å, and the thiospinel becomes nearly stoichiometric $CuCo_2S_4$, although a secondary phase of slightly Cu-doped CoS_2 forms. Bulk SC at 4.2 K and Pauli paramagnetism have been demonstrated for the sulfurized $CuCo_2S_4$ by the measurements of electrical resistivity, magnetic susceptibility, and specific heat.

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I. INTRODUCTION

The discoveries of superconductivity (SC) in the complex copper oxide [1] and the iron-based pnictide [2] stimulate enthusiasm to search for SC especially in late 3d-transition-metal (Fe, Co, Ni, and Cu) compounds [3–7]. Among them, the Co-based superconductors are very limited so far. One example is the cobalt oxyhydrate $Na_xCoO_2 \cdot yH_2O$ ($x \approx 0.35, y \approx 1.3$), which shows SC at $T_c \approx 4.5$ K [8]. The Co-based thiospinel $CuCo_2S_4$ shows similarities with $Na_xCoO_2 \cdot yH_2O$ in the Co coordination, geometrical frustration, and formal Co valence. However, it is not clear whether $CuCo_2S_4$ superconducts or not. Besides, the magnetism of $CuCo_2S_4$ also remains elusive up to present.

Earlier studies in the 1960s suggested Pauli paramagnetism in $CuCo_2S_4$ [9,10], and no SC transition was observed down to 0.05 K [11]. In the 1990s, however, it was reported that $CuCo_2S_4$ shows a Curie-Weiss (CW) paramagnetism with an effective magnetic moment of $0.89\,\mu_B$ per formula unit (f.u.) [12]. A cusp in the magnetic susceptibility appears at $T_N = 18$ K, which was attributed to an antiferromagnetic spin ordering. In a multiphasic sample with the nominal composition of $Cu_{1.5}Co_{1.5}S_4$, SC or SC-like behavior was observed with an onset transition temperature of $T_c^{\text{onset}} = 4.0$ K and a zero-resistance temperature of $T_c^{\text{zero}} = 2.3$ K. Investigations on the ^{63}Cu and ^{59}Co NMR suggested a gapless SC state as well as antiferromagnetic spin correlations, and SC was considered to be in line with the growth of antiferromagnetic spin correlation [13]. Contrastingly, a later NMR study on the Co-rich series samples of $(Cu_xCo_{1-x})Co_2S_4$ indicated a full SC gap without long-range magnetic ordering for $CuCo_2S_4$ [14]. It was concluded that SC and the antiferromagnetic spin correlation are associated with the Co-3d and Cu-3d holes, respectively.

One of the present authors (G.-H.C.) and coworkers [15] attempted to reproduce SC in $CuCo_2S_4$ in 2003. However, no SC was observed above 1.8 K in the single-phase sample of $CuCo_2S_4$, although signature of SC at $T_c = 3.5$ K was detected in a multiphasic sample. Aito and Sato [16] reported the resistivity data of five $CuCo_2S_4$ samples from different batches. Two of them showed a SC transition, and the higher T_c value is 3.8 K. Fang *et al.* [17] synthesized an unusual K-doped sample $Cu_{1.3}K_{0.2}Co_{1.5}S_4$ which showed SC at 4.4 K together with a CW-like susceptibility but without any antiferromagnetic transition down to 9 K. A very recent work [18] showed an absence of SC with a weak antiferromagnetic transition at about 4 K in $CuCo_2S_4$. In a word, the previous reports on $CuCo_2S_4$ appear to be highly dispersive and even contradictive. To our knowledge, evidence of bulk SC with specific-heat measurements has not been reported so far in the Cu-Co-S system.

The contradictive results above strongly suggest that the physical properties are sensitive to the synthesis of samples, and a controlled preparation of nearly stoichiometric samples of $CuCo_2S_4$ is crucial to clarify the intrinsic properties. Previous studies showed difficulties in obtaining desired samples of $CuCo_2S_4$ [12,15,16,19–21]. They were commonly synthesized by direct reacting copper and cobalt powders with sulfur in a sealed evacuated silica tube at an elevated temperatures. While relatively low reaction temperatures (500–600 °C) were suggested for the preparation of monophasic $CuCo_2S_4$ [22], a follow-up work [19] failed to obtain the single-phase sample. The synthesized sample tends to form CoS_2 impurity, as revealed by the phase-relation study in the Cu-Co-S system [20,21]. Indeed, later studies [12,14–16] also showed the presence of the CoS_2 impurity for the reaction temperatures from 500 to 800 °C. Note that CoS_2 is a ferromagnet with a

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Curie temperature of ∼120 K [23–25], which makes it more easily detectable by the magnetic measurement [15].

Here we report a novel two-step strategy for the controlled synthesis of stoichiometric $CuCo_2S_4$. First, to minimize the formation of CoS_2 impurity, we prepared sulfur-deficient $CuCo_2S_{4-\delta}$ with $\delta = 0.3$. Then, the S-deficient sample was sulfurized by annealing in the presence of an appropriate amount of sulfur. As a result, the main phase of the annealed sample was found to be nearly stoichiometric $CuCo_2S_4$. Bulk SC at 4.2 K and Pauli paramagnetism in the normal state were demonstrated in the S-compensated $CuCo_2S_4$.

II. EXPERIMENTAL METHODS

A polycrystalline sample of S-deficient $CuCo_2S_{3.7}$ was first prepared by high-temperature reactions of the constituent elements in a sealed evacuated silica tube. The source materials were powders of copper (99.997%), cobalt (99.998%), and sulfur (99.999%). The homogenized mixture with the composition of $CuCo_2S_{3.7}$ was allowed to fire at 750 °C for 72 h. This procedure was repeated to improve the quality of the sample. In the second step, the synthesized $CuCo_2S_{3.7}$ was sulfurized in the presence of compensatory sulfur (0.35 S/f.u.) by annealing at 450 °C for 144 h in a sealed evacuated silica ampoule. Note that an excess of sulfur was necessary to ensure a full sulfurization. This is because, during the sulfurization, a side reaction that forms CoS_2 always takes place, which additionally consumes sulfur. Besides, in order to quantize the amount of the CoS_2 impurity in the sulfurized sample, we additionally prepared CoS_2 by reacting Co with S in an evacuated silica tube. The sample is of single phase with the lattice constant of $a = 5.535$ Å (consistent with the previous report [23]), as determined by the powder x-ray diffractions (XRD).

Powder XRD were carried out using a PANalytical diffractometer (Empyrean Series 2) with a monochromatic Cu-$K_{\alpha1}$ radiation. The crystal structure were refined by a Rietveld analysis using the GSAS+EXPGUI package [26]. The sulfur content in the crystallites was examined by energy-dispersive x-ray spectroscopy (EDS, Oxford Instruments X-Max) equipped in a scanning electron microscope (SEM, Hitachi S-3700N).

The electrical resistivity and specific heat were measured on a Quantum Design Physical Properties Measurement System, and the magnetic properties were measured on a Quantum Design Magnetic Property Measurement System. The resistivity measurement employed a standard four-terminal method. The heat-capacity measurement utilized a thermal relaxation technique. In the magnetic measurements, the applied magnetic fields were set to be 20 and 10,000 Oe, respectively, to detect SC and to study the normal-state magnetism. In the case of the low-field measurements, both zero-field-cooling (ZFC) and field-cooling (FC) protocols were employed.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the XRD profile for the sulfur-deficient sample of $CuCo_2S_{3.7}$. Most of the reflections can be well indexed with a face-centered cubic unit cell of the thiospinel. As is seen in the inset, no reflections associated with CoS_2 are detectable, while a tiny amount of Cu_2S is possibly presented. Therefore, with a lack of sulfur we succeeded in avoiding the appearance of the CoS_2 secondary phase. The Rietveld refinement ($R_{\mathrm{wp}} = 2.3\%$ and $\chi^2 = 1.31$) confirms the normal spinel structure with $a = 9.4544(1)$ Å and $u = 0.3865(1)$ for the main phase. Note that the lattice constant is the smallest among those reported previously for $CuCo_2S_4$ {9.461(2) Å [22], 9.478(5) Å [19], and 9.472(1) Å [20]}. This may be attributed the apparent sulfur deficiency and/or the partial substitution of Cu by Co (hereafter denoted as Co/Cu substitution) [14]. The latter is implied by the presence of a small amount of Cu_2S. As a matter of fact, the Rietveld refinement does not support a significant sulfur vacancy.

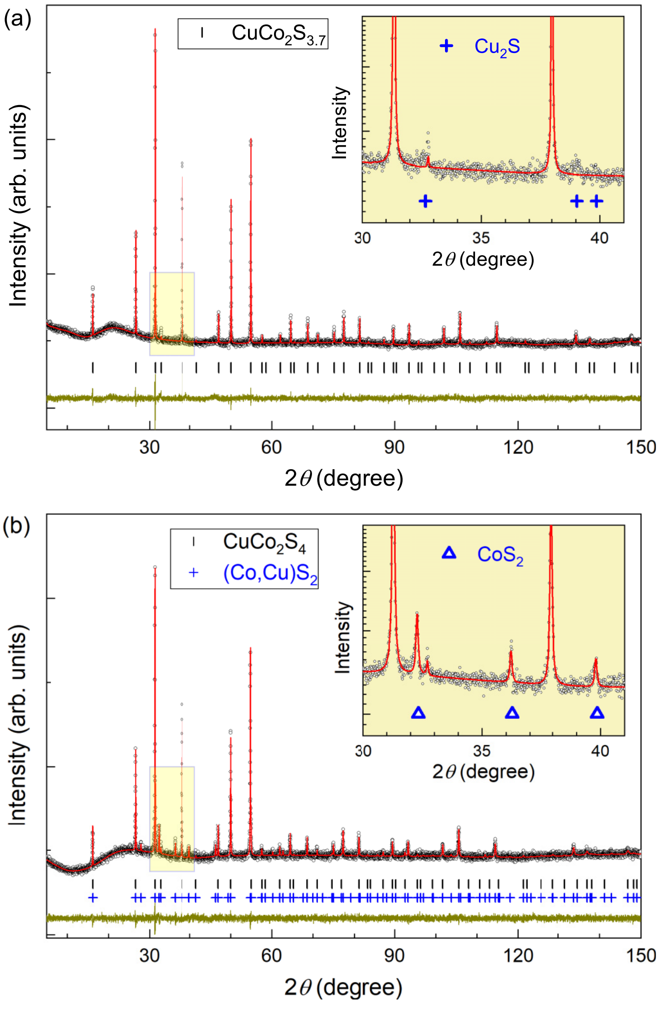

FIG. 1. Powder XRD with the Rietveld refinement profiles for samples of sulfur-deficient $CuCo_2S_{3.7}$ (a) and sulfurized $CuCo_2S_4$ (b). The insets (with a logarithmic scale for the intensity) are a close-up of the marked area, which shows the presence of the secondary phases of Cu_2S and CoS_2, respectively, in $CuCo_2S_{3.7}$ and sulfurized $CuCo_2S_4$.

The XRD pattern of the sulfurized $CuCo_2S_4$ is displayed in Fig. 1(b). The main phase remains to be the cubic thiospinel, although a small amount of CoS_2-like phase emerges. With the two-phase Rietveld refinement ($R_{\mathrm{wp}} = 2.2\%$ and $\chi^2 = 1.13$), the weight percentage of the CoS_2-like impurity was

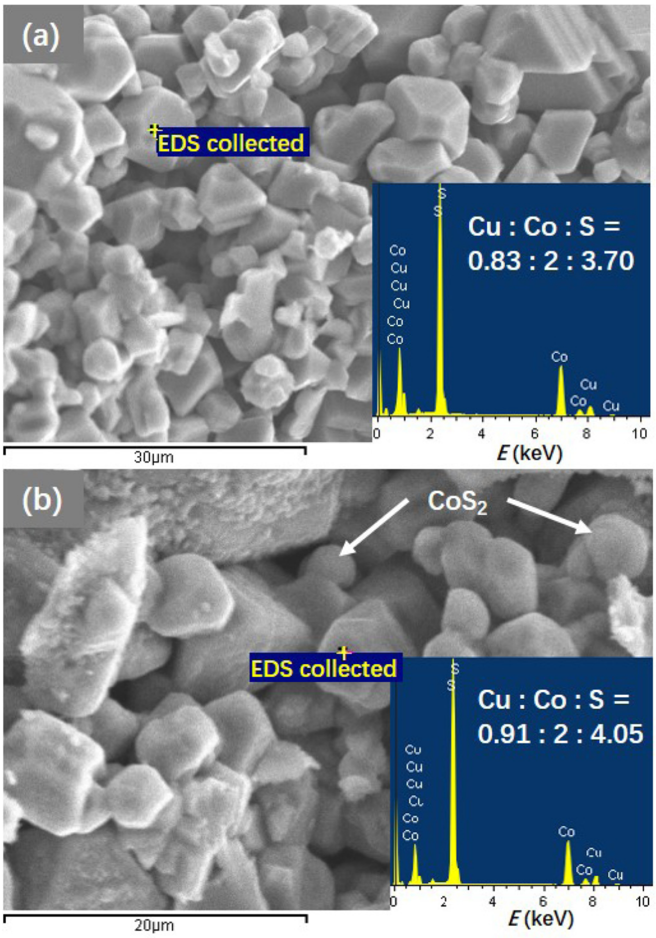

FIG. 2. Typical SEM images of sulfur-deficient $CuCo_2S_{3.7}$ (a) and sulfurized $CuCo_2S_4$ (b). The lower-right insets are the EDS collected with the electron beam focused on the spots marked. Round-shape grains (indicated by arrows) can be seen in (b), which are identified to be lightly Cu-doped CoS_2. The atomic ratios are given by the EDS analysis.

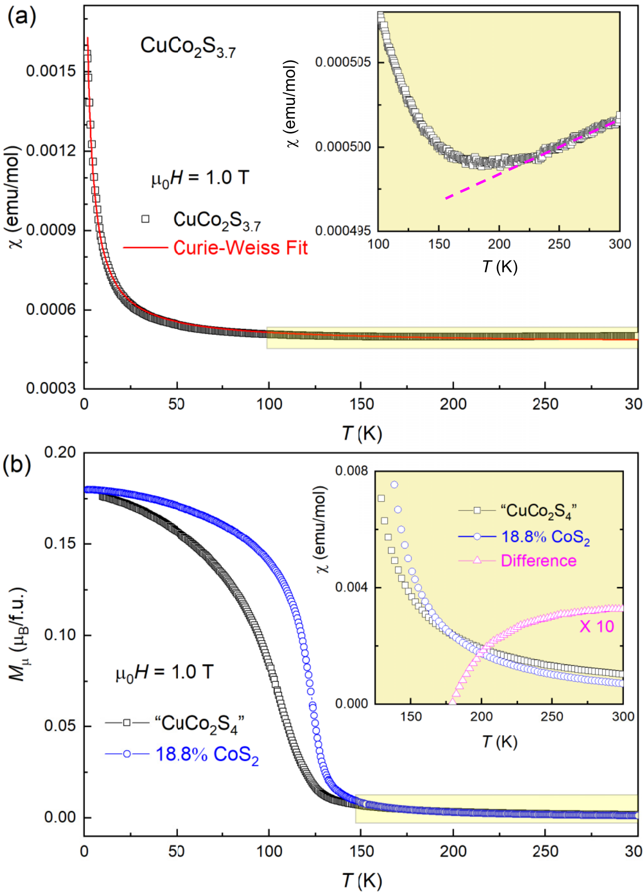

FIG. 3. Temperature dependence of magnetic susceptibility or magnetization for sulfur-deficient $CuCo_2S_{3.7}$ (a) and sulfurized $CuCo_2S_4$ (b). The inset of (a) is a close-up of the high-temperature data, indicating a positive-temperature-coefficient behavior (dashed line). In (b), the magnetization of CoS_2 (multiplied by a factor of 18.8%) is plotted for comparison. The inset of (b) compares the magnetic susceptibilities at high temperatures.

determined to be 14.8(6)%. The lattice constant of the pyrite phase is refined to be 5.538(1) Å, which is slightly larger than that of CoS_2 (5.534 Å [23]), suggesting that Cu is slightly incorporated. The structural parameters of the main phase were fitted to be $a = 9.4750(2)$ Å and $u = 0.3851(1)$. The a axis is remarkably larger than that of the sulfur-deficient $CuCo_2S_{3.7}$, suggesting a successful sulfurization.

The two samples above were examined by SEM observations in combination with the EDS measurements. As shown in Fig. 2(a), the crystallites of S-deficient $CuCo_2S_{3.7}$ are similar in shape. The sulfur content, measured on the basis of the Co content, is consistent with the nominal composition. However, the Cu content is substantially lower than the nominal one. The result suggests that the real composition of the thiospinel phase is something like $(Cu_{1-x-y}Co_x)Co_2S_{4-\delta}$. The SEM image of the sulfurized sample [Fig. 2(b)] shows additional round-shape crystallites which were identified to be slightly Cu-doped CoS_2 (1-2% Cu) by the EDS analysis. Furthermore, the sulfur deficiency is fully compensated, and the Cu content is also increased, as is indicated by the atomic ratio measured. Therefore, we conclude that the sulfurized sample mainly (~85% by weight) contains nearly stoichiometric $CuCo_2S_4$.

Figure 3(a) shows the temperature dependence of magnetic susceptibility under a magnetic field of $H = 10$ kOe for the sulfur-deficient $CuCo_2S_{3.7}$. The magnetic susceptibility is nearly temperature independent at high temperatures. No anomaly at ~120 K can be seen, indicating free of the ferromagnetic impurity of CoS_2. There is an upturn tail at low temperatures. Fitting of the data with the CW formula, $\chi = \chi_0 + C/(T - \theta_{CW})$, yields a temperature-independent term of $\chi_0 = 0.00047$ emu mol-f.u.$^{-1}$, a Curie constant of $C = 0.0043$ emu K mol-f.u.$^{-1}$, and a paramagnetic CW temperature of $\theta_{CW} = -1.9$ K. Such a small value of the Curie constant (corresponding to $0.13\mu_B$/Co) is commonly originated from tiny paramagnetic impurities. Additionally, the positive temperature coefficient of susceptibility at high temperatures, shown in the inset of Fig. 3(a), also rules out the possible CW-type paramagnetism in $CuCo_2S_{3.7}$.

Figure 3(b) shows the temperature dependence of magnetization (in the unit of μ_B/f.u.) of the sulfurized $CuCo_2S_4$ under the same magnetic field of $H = 10$ kOe. A

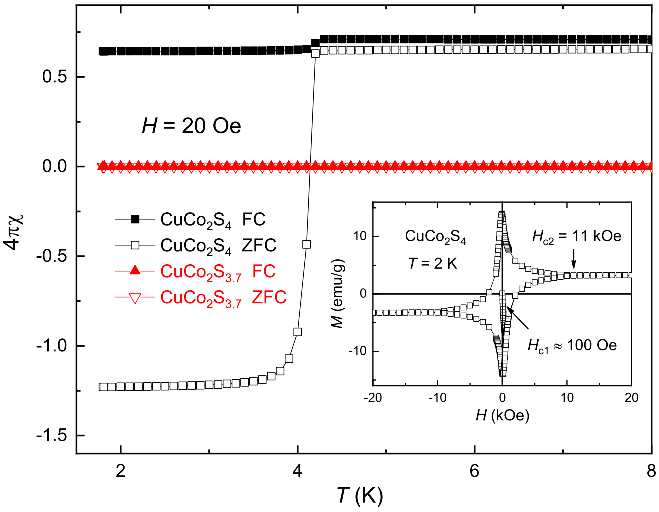

FIG. 4. Temperature dependence of magnetic susceptibility for sulfur-deficient CuCo$_2$S$_{3.7}$, as well as sulfurized CuCo$_2$S$_4$, measured under a magnetic field of 20 Oe in both FC and ZFC modes. The inset shows field dependence of magnetization at 2 K for sulfurized CuCo$_2$S$_4$.

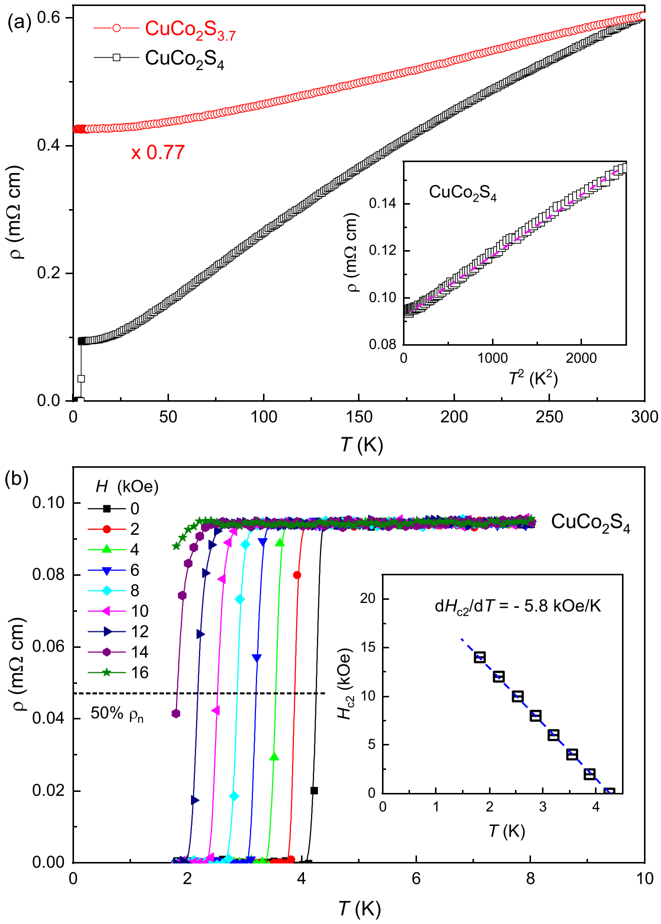

FIG. 5. (a) Temperature dependence of electrical resistivity (ρ) of the polycrystalline samples of sulfur-deficient CuCo$_2$S$_{3.7}$ and sulfurized CuCo$_2$S$_4$. The inset plots ρ versus T^2 in the temperature range from 4.5 to 50 K. (b) Resistive superconducting transitions under increased magnetic fields from which the upper critical fields H_{c2} were obtained. The inset plots the resultant H_{c2} as a function of temperature.

ferromagnetic transition is seen at about 120 K, which is attributed to the ferromagnetic impurity of slightly Cu-doped CoS$_2$ that was identified by the XRD experiment above. To quantify the amount of (Co, Cu)S$_2$ independently, the magnetization data of pure CoS$_2$ are shown for comparison. One sees that the Curie temperature of (Co, Cu)S$_2$ is slightly lower than that of CoS$_2$ due to the Cu incorporation. The low-temperature saturation magnetization is about 19% of that CoS$_2$. At the same time, the high-temperature magnetic susceptibility basically coincides. Since the Cu content in (Co, Cu)S$_2$ is only 1–2% according to the EDS measurement, the amount of the (Co, Cu)S$_2$ impurity should be also around 19%, basically consistent with the XRD result above.

The high-temperature magnetic susceptibility data are highlighted in the inset of Fig. 3(b), which shows a CW-type paramagnetism. The CW paramagnetism is attributed to the (Co, Cu)S$_2$ impurity, because the magnetic susceptibility of the sulfurized CuCo$_2$S$_4$ shows a similar temperature dependence with that of 18.8% CoS$_2$. The magnetic susceptibility of S-compensated CuCo$_2$S$_4$ phase can be roughly obtained by a simple substraction. The result indicates a small value of magnetic susceptibility that is almost temperature independent. Therefore, CuCo$_2$S$_4$ should be intrinsically Pauli paramagnetic. Nevertheless, the accurate value of the Pauli-paramagnetic susceptibility cannot be reliably extracted not only because of the influence of the magnetic impurity but also because of the possible Van Vleck paramagnetism involved [10]. According to the band-structure calculation of CuCo$_2$S$_4$ which gives the density of states at Fermi level of 31.88 states/eV/f.u. [27], the calculated Pauli-paramagnetic susceptibility is derived to be $\chi_{\rm P} = \mu_{\rm B}^2 N(E_{\rm F}) = 1.03 \times 10^{-3}$ cm^3/mol.

Figure 4 shows the low-temperature susceptibility data for the samples of CuCo$_2$S$_{3.7}$ as well as sulfurized CuCo$_2$S$_4$. The S-deficient CuCo$_2$S$_{3.7}$ exhibits low values of magnetic susceptibility, and no signal of SC can be detected down to 1.8 K. By contrast, the sulfurized sample shows a steep decrease in the magnetic susceptibility at 4.2 K, suggesting a SC transition. Note that the high value of the susceptibility above $T_{\rm c}$ is due to the ferromagnetic impurity (Co, Cu)S$_2$. The large magnitude of the ZFC diamagnetism (exceeding -100%) below $T_{\rm c}$ could also be due to the extra magnetic field generated by the ferromagnetic (Co, Cu)S$_2$. The inset shows the field dependence of magnetization at 2 K for the SC sample. An extremely type-II SC with $H_{c2} \gg H_{c1}$ can be concluded. As expected also, the ferromagnetic signal from (Co, Cu)S$_2$ is superposed on the SC loop.

Figure 5(a) shows the temperature dependence of resistivity for the sulfur-deficient CuCo$_2$S$_{3.7}$ and the sulfurized CuCo$_2$S$_4$. Both samples show a metallic behavior, yet the sulfurized CuCo$_2$S$_4$ sample exhibits a lower room-temperature resistivity with a higher residual resistivity ratio (RRR). The RRR values are 1.4 and 6.4 for CuCo$_2$S$_{3.7}$ and CuCo$_2$S$_4$, respectively. Although there are about 19% (Co, Cu)S$_2$ impurity in the sulfurized CuCo$_2$S$_4$ sample, no anomaly at ∼120 K associated with the ferromagnetic transition can be detected.

At lower temperatures, while no SC transition appears down to 1.8 K for $CuCo_2S_{3.7}$, a sharp SC transition is seen at $T_c^{onset} = 4.3$ K for the S-compensated $CuCo_2S_4$. The observation of SC in relation with a high RRR value was also reported previously [16]. This could suggest that the nonmagnetic scattering, measured by the residual resistivity, may destroy SC in the system, resembling the scenario in Sr_2RuO_4 [28] and $K_2Cr_3As_3$ [29]. Besides, the low-temperature resistivity of $CuCo_2S_4$ essentially shows a T^2 temperature dependence (see the inset), suggesting dominant electron-electron scattering in the system.

The resistive SC transitions are more clearly shown in Fig. 5(b). One sees that the SC transition shifts to lower temperatures with increasing magnetic fields. Using the criterion of 50% normal-state resistivity just above T_c for determining $T_c(H)$, the upper critical magnetic fields H_{c2} can be extracted. The resultant $H_{c2}(T)$ data are shown in the inset of Fig. 5(b), which shows an essentially linear temperature dependence down to $0.42T_c$. This result suggests a dominant orbital pair-breaking mechanism over a paramagnetic pair-breaking mechanism. The zero-temperature upper critical field is estimated to be $H_{c2}(0) = 24.6$ kOe from the linear extrapolation, far below the Pauli-paramagnetic limit $H_P \approx 77$ kOe. The coherence length can thus be derived as $\xi_0 = 11.6$ nm using the relation $H_{c2}(0) = \Phi_0/[2\pi\xi(0)^2]$, where $\Phi_0 (= 2.07 \times 10^{-15}$ Wb) denotes a magnetic flux quantum.

Figure 6(a) shows the temperature dependence of specific heat for the sulfurized $CuCo_2S_4$ sample. The specific heat tends to approach the value of $3NR = 174.6$ J K^{-1} mol^{-1} at high temperatures, in accordance with the Dulong-Petit law. No obvious anomaly is seen at around 120 K where the CoS_2 impurity undergoes a ferromagnetic transition. This observation verifies that the CoS_2 impurity is the minor phase. As is seen in the inset of Fig. 6(a), at low temperatures, a remarkable specific-heat jump is observable at around 4 K, confirming bulk SC in the sulfurized sample which dominantly contains nearly stoichiometric $CuCo_2S_4$.

Figure 6(b) shows the plot of C/T versus T^2, from which the low-temperature electronic specific heat can be separated out. The linear fit gives an intercept of $\gamma = 32.2$ mJ K^{-2} mol-f.u.$^{-1}$, corresponding to a bare density of states of $N(E_F) = 3\gamma/(\pi^2 k_B^2) = 13.6$ states/eV/f.u., consistent with the electronic structure calculation [27]. Note that the Sommerfeld constant of CoS_2 is 21 mJ K^{-2} mol^{-1} [24,25], somewhat smaller than the above γ value, yet it turns out to be larger on the basis of Co content. Furthermore, the CoS_2 impurity is the minor phase after all. Therefore, the Sommerfeld coefficient of the $CuCo_2S_4$ phase will not change very much even if corrections due to the existence of CoS_2 impurity could be reliably made.

Assuming the γ value of 32.2 mJ K^{-2} mol-f.u.$^{-1}$ and with the electronic specific heat of $C_e = C - \beta T^3$, Fig. 6(c) was plotted using $C_e/(\gamma T)$ and T/T_c as the coordinates. Under the constraint of entropy conservation, i.e., $\int_0^{T_c} [(C_e - \gamma T)/T] dT = 0$, a full-gap BCS α model [30] can basically fit the data with $\alpha \equiv \Delta(0)/(k_B T_c) = 1.5$ if a residual electronic specific-heat coefficient of $\gamma_0 = 0.25\gamma$ due to the existence of a non-SC impurity phase of CoS_2 is taken into account. In this circumstance, the SC fraction is fitted to be 77(1)%, which is conversely consistent with ∼19% non-SC phase.

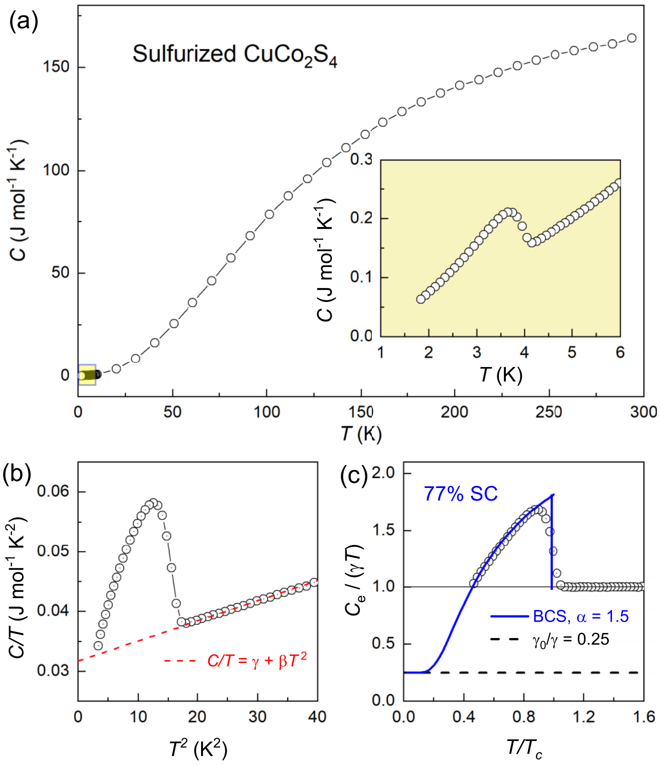

FIG. 6. Temperature dependence of specific heat for sulfurized $CuCo_2S_4$. The inset of (a) shows a close-up in the low-temperature region. Panel (b) plots C/T as a function of T^2, in which a linear fit ($C/T = \gamma + \beta T^2$) is presented for the normal state. Panel (c) shows $C_e/(\gamma T)$, where $C_e = C - \beta T^3$ denotes the electronic specific heat as a function of the reduced temperature, T/T_c. The data basically agree with a full-gap BCS α model [$\alpha \equiv \Delta(0)/(k_B T_c)$, where $\Delta(0)$ is the anisotropic superconducting gap at zero temperature] [30] assuming 77% superconducting phase and a residual electronic specific-heat coefficient of $\gamma_0 = 0.25\gamma$.

Here we note that the single-gap BCS model does not account for the data exclusively. Other models with line energy-gap nodes are also applicable. However, the present limited data cannot distinguish which model applies. Interestingly, previous NMR investigations concluded contrasting SC properties in the Cu-Co-S system: One suggested a gapless SC state [13]; the other indicated a full SC gap [14]. This discrepancy seems to be due to the big difference in the sample's quality. Our present specific-heat result excludes the possibility of gapless SC in the nearly stoichiometric sample of $CuCo_2S_4$. We expect that future measurements of specific-heat, NMR, and other techniques down to lower temperatures with using better samples (with less impurity) will be able to clarify the issue of the SC gap.

Above we have clarified that the nearly stoichiometric $CuCo_2S_4$ thiospinel is a SC with Pauli paramagnetism. Now let us comment on the previous dispersive results about "$CuCo_2S_4$" [11,12,15,16,18]. They can be accounted for in terms of the deviations from the stoichiometry. The actual composition of the synthesized thiospinel phase should be written as $(Cu_{1-x}Co_x)Co_2S_{4-\delta}$ (because impurity phases such as CoS_2 and Cu_2S appeared). The S deficiency obviously decreases the hole concentration in $(Cu_{1-x}Co_x)Co_2S_{4-\delta}$, which suppresses SC. The Co/Cu substitution (Co^{2+} partially substitutes Cu^+) not only decreases the hole concentration but also possibly induces magnetic impurity of Co^{2+} at the Cu site, both of which are detrimental to SC. This could be the main reason for the difficulty in observing SC in the sample with nominally stoichiometric composition. In the Cu-rich sample of "$Cu_{1.5}Co_{1.5}S_4$" [13,14], however, the Co/Cu substitution at the Cu site is greatly reduced because Co is poor. The possible Cu occupation at the Co site may not destroy SC because of nonmagnetic Cu^+. Thus SC is easily observed in the Cu-rich samples.

IV. CONCLUDING REMARKS

To summarize, with a novel two-step synthesis strategy, we were able to prepare a nearly stoichiometric $CuCo_2S_4$ phase which shows bulk SC at 4.2 K with Pauli paramagnetism in the normal state. We have also revealed that sulfur deficiency and Co/Cu substitution is detrimental to SC, which may explain the contradictive results in previous reports. The result calls for further investigations on the rare Co-based SC by optimizing the sample quality (with the CoS_2 impurity as less as possible) and with various measurements down to lower temperatures.

SC in Co-based compounds is very rare. This work corroborates that $CuCo_2S_4$ is another Co-based superconductor in addition to $Na_xCoO_2 \cdot yH_2O$ [8]. Albeit of different crystal structures, interestingly, the two systems show many similarities including the T_c value, Co coordination, formal Co valence, and the geometrical frustration. It is of great interest to clarify whether $CuCo_2S_4$ is an unconventional SC [31]. On the other hand, SC is not frequently found in the thiospinel compounds. However, the CuM_2S_4 (M = Co, Rh, or Ir) family seems to be the only exception. $CuRh_2S_4$ was first discovered to be a SC in 1967 with $T_c = 4.35-4.8$ K [11,32], which was confirmed in the 1990s [33]. $CuIr_2S_4$ [34] itself is not a superconductor, yet it undergoes a metal-insulator transition at 230 K accompanied with a charge ordering as well as a spin dimerization [35]. SC with T_c up to 3.4 K can be induced by the suppression of the metal-insulator transition via Zn/Cu substitution [36,37]. For the spinel selenides, SC was reported in $CuRh_2Se_4$ ($T_c = 3.5$ K [11,32]) and $Cu(Ir_{0.8}Pt_{0.2})_2Se_4$ ($T_c = 1.76$ K [38]). Therefore, one may expect that $CuCo_2Se_4$ could be also a SC if it can be synthesized with the stoichiometric composition.

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