Superconductivity in thiospinel $Cu_{1.3}K_{0.2}Co_{1.5}S_4$

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We succeeded in substituting slight K for Cu in the parent thiospinel material $Cu_{1.5}Co_{1.5}S_4$. It is found that $Cu_{1.3}K_{0.2}Co_{1.5}S_4$ undergoes a superconducting transition at 4.4 K, and no antiferromagnetism was observed around 20 K, which was supposed to be one of the characteristics of superconductor $Cu_{1.5}Co_{1.5}S_4$ ($T_c \sim 4.0$ K). We conclude that the antiferromagnetism of thiospinel $Cu_{1.5}Co_{1.5}S_4$ may stem from tetrahedral A site occupied by Cu atoms and there is no direct relationship between superconductivity and antiferromagnetism.

I. INTRODUCTION

Thiospinel compound CuM_2S_4 (M=Co, Rh, and Ir) has been extensively studied for many physical properties in the past decades. $CuRh_2S_4$ is a superconductor below 4.7 K,[1] $CuIr_2S_4$ is well known for the presence of a metal-insulator transition at 230 K accompanied by the loss of localized magnetic moments, and changes into a superconducting state when Zn partially substitutes for Cu at low temperatures.[2–6] More recently, spin dimerization in the spinel $CuIr_2S_4$ was found by Radalli *et al.*[7] As to the spinel $CuCo_2S_4$, it is controversial about its superconductivity. Furukawa *et al.* concluded that $CuCo_2S_4$ is not a superconductor.[8] However Wada *et al.* claimed that they synthesized a stoichiometric $CuCo_2S_4$ compound, which shows a rather high T_c of superconductivity at 4.4 K with a very sharp transition width ($\approx$0.1 K) and a perfect Meissner fraction,[10] but no direct experiment data of superconductivity were provided. Among those compounds, researchers paid much attention to the thiospinel $Cu_{1+x}Co_{2-x}S_4$ with a nominal Cu composition x=0–0.5 because of the possible incidence of antiferromagnetism on the superconducting state. This compound has a Curie-Weiss-type susceptibility with an AF behavior below T_N (about 19 K) and a SC transition at the lower temperature T_c (T_c^{onset}=4.0 K).[8]

In the case of $Cu_{1.5}Co_{1.5}S_4$, it is considered that the effect of additional Cu atoms substitute for the Co atoms at the octahedral B site, and the ionic distribution is given by $Cu^{2+}[Cu_{0.5}^{2+}Co_{1.5}^{3+}]S_{4-\delta}$, the Cu atoms are in the $Cu^{2+}(3d^9)$ ionic state,[9] which is similar to ionic state of Cu atoms in copper oxide high temperature superconductors (HTSC). Nuclear-magnetic-resonance (NMR) study shows further similarity to those observed in high-T_c copper oxide, which are associated with the emergence and enhancement of antiferromagnetic spin correlations at low temperatures.[8] But Wada *et al.* concluded that, as to spinel compounds $(Cu_xCo_{1-x})Co_2S_4$, the appearance of superconductivity in the Cu-rich region originates from the significant increase in $N(E_F)$ associated with Co on the octahedral B site, and the development of the AF spin correlation originates from the increase in $N(E_F)$ associated with Cu on the tetrahedral A

site.[10] Obviously the conclusion from Wada is in contrast with the interplay between superconductivity and antiferromagnetism. So it is worth studying the possible incidence of antiferromagnetism on the superconducting state.

In this paper, slight potassium was used to substitute Cu on the parent phase $Cu_{1.5}Co_{1.5}S_4$. It is found that the antiferromagnetism is destroyed by the substitution of potassium and no clear change of superconducting transition temperature is observed.

II. EXPERIMENT

Polycrystalline samples of $Cu_{1.3}K_{0.2}Co_{1.5}S_4$ were prepared by chemical reaction in sealed evacuated quartz tubes. The starting materials were CuS, Co, K_2CO_3, and S with purity higher than 99.9%. They were mixed stoichiometrically and pressed into pellet after thorough grounding, finally the pellet was sealed in an evacuated quartz tube. The tube was heated slowly to 1073 K and then sintered for 48 hours. Taking account of the oxygen in K_2CO_3, a slight excess sulfur is required to synthesize a single phase. The preparation of $Cu_{1.3}K_{0.2}Co_{1.5}S_4$ and the undoped sample $Cu_{1.5}Co_{1.5}S_4$ was repeated for many times. It is quite easy to reproduce the samples with the same quality (the same superconducting transition width and the x-ray diffraction pattern) if the pressure for making the pellet and the synthesizing temperature are appropriate. Powder XRD was performed at room temperature employing a M18AHF x-ray diffractometer (MAC Science). The magnetic measurements were carried out with an Oxford multiparameter measurement setup (Maglab-12) and a quantum design superconducting quantum interference device (SQUID MPMS-5). The electrical resistivity was measured by the four-probe method based on Maglab-12 system. The microscopic analysis is achieved with EDAX of scanning electron microscopy (Oxford).

III. RESULTS AND DISCUSSION

A. X-ray powder diffraction

Figure 1 presents the x-ray diffraction patterns at room temperature for samples $Cu_{1.5}Co_{1.5}S_4$ and $Cu_{1.3}K_{0.2}Co_{1.5}S_4$.
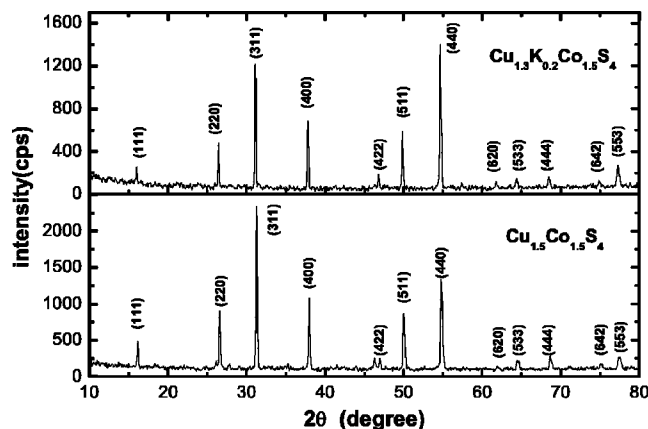
FIG. 1. X-ray diffraction patterns of $Cu_{1.5}Co_{1.5}S_4$ and $Cu_{1.3}K_{0.2}Co_{1.5}S_4$.

All the diffraction peaks have indexed to the cubic unit cell. These indexed peaks have (h,k,l) values that are either all even or all odd, which are consistent with a fcc unit cell. Based on the XRD patterns, it is concluded that both samples are close to single phase.

B. EDAX of SEM

Owing to the slight potassium we doped, one of the possibilities for the nice XRD is that potassium ions exist as impurity and the x-ray diffraction peaks of potassium second phase are so weak that they were prevailed by the peaks of $Cu_{1+x}Co_{2-x}S_4$ and even the background. Therefore it is necessary to seek further evidence to prove that the potassium ions indeed enter the cell of $Cu_{1+x}Co_{2-x}S_4$. We selected several grains (could be typical crystals) from our sample and analyzed with EDAX of SEM, the spectrum revealed that the potassium ions indeed enter into the cell of $Cu_{1+x}Co_{2-x}S_4$. Figure 2 is the spectrum of EDAX which was taken on a clean surface of a small crystal as shown in Fig. 3 for a typical crystal. Similar amount of K was discovered on other grains.

As to $Cu_{1.5}Co_{1.5}S_4$, the effect of additional Cu atoms is believed to substitute for the Co atoms at the octahedral B site, so when K substitutes Cu, it is possible that potassium
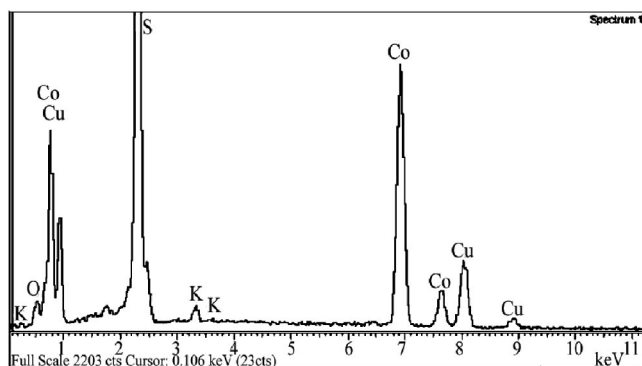

FIG. 2. EDAX spectrum of a typical crystal of spinel $Cu_{1.3}K_{0.2}Co_{1.5}S_4$.

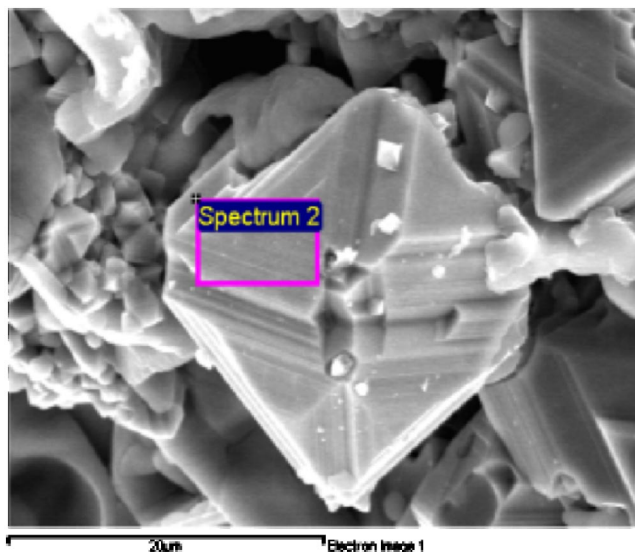
FIG. 3. The analyzed region on a $Cu_{2-x}K_xCo_{1.5}S_4$ crystal. The rectangle marks the region where we get the EDAX spectrum.

atoms occupy both the tetrahedral A site and octahedral B site.

C. Diamagnetic measurement

AC susceptibility is a stringent test of the superconducting properties. Figure 4 shows the ac-magnetic susceptibility for the sintered bulk sample of $Cu_{1.3}K_{0.2}Co_{1.5}S_4$. Sharp transition reveals again the single phase of our sample. The transition temperature in the susceptibility is 4.4 K, which is defined by the onset point of the real part of ac susceptibility.

Figure 5 is the ac susceptibility under different dc magnetic fields. The transition curve moves parallel down to lower temperatures with increasing field. Taking account of the dirty limit, the $H_{c2}(0)$ can be obtained by the Werthamer-Helfand-Hohenberg (WHH) formula[11]
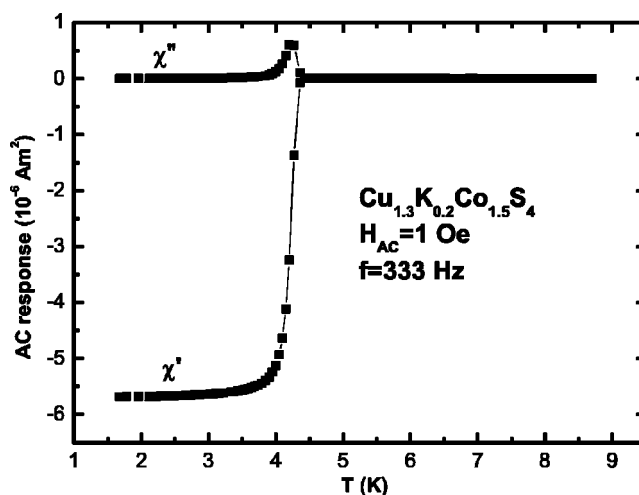

FIG. 4. ac susceptibility as a function of temperature for the sample $Cu_{1.3}K_{0.2}Co_{1.5}S_4$.

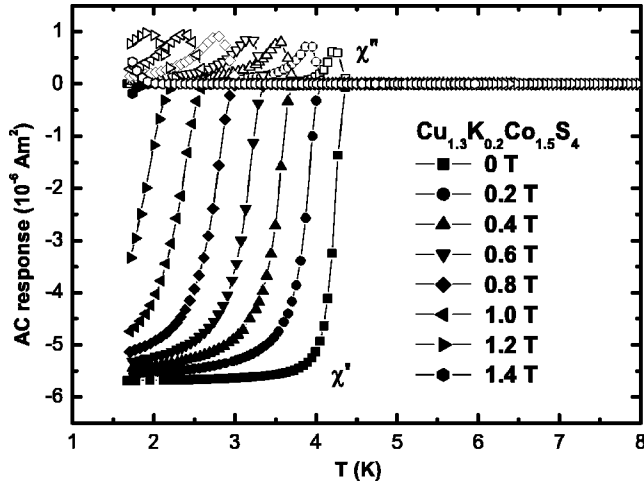FIG. 5. ac susceptibility under different magnetic fields for the sample Cu$_{1.3}$K$_{0.2}$Co$_{1.5}$S$_4$.

$$H_{c2}(0) = -0.693 T_c \left(\frac{dH_{c2}}{dT} \right)_{T=T_c}. \qquad (1)$$

In this way the upper critical field is about 18.9 kOe, which is consistent with the upper critical field of CuCo$_2$S$_4$ [$H_{c2}(0) \approx 19$ kOe] reported by Wada *et al.*[10]

D. Electrical resistivity measurement

Figure 6 depicts the change of resistivity under various magnetic fields. Decreasing temperature from 8 K to 4.6 K under zero field, the resistivity ρ changes subtly, and an abrupt superconducting transition happens at 4.54 K, zero resistivity is obtained below 4.37 K. Sharp transition less than 0.2 K indicates that the sample we prepared is of single phase, which is consistent with the XRD pattern and ac susceptibility of Cu$_{1.3}$K$_{0.2}$Co$_{1.5}$S$_4$. The superconducting transition shifts almost parallel down to lower temperatures with increasing magnetic field. According to WHH theory,[11] the upper critical field is 18.8 kOe derived from resistivity mea-
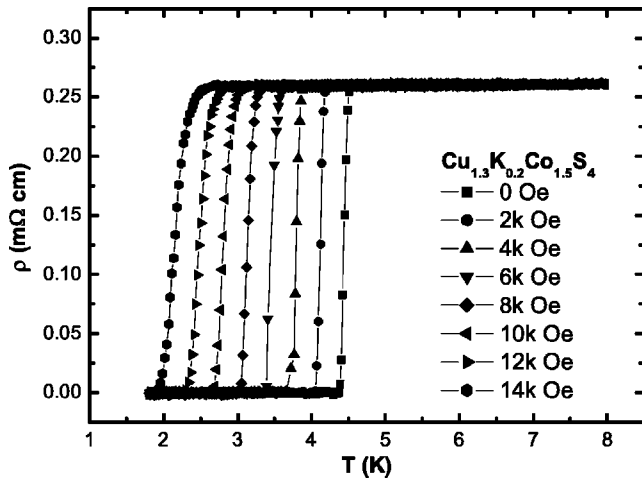

FIG. 6. Temperature dependence of resistivity of Cu$_{1.3}$K$_{0.2}$Co$_{1.5}$S$_4$ under various magnetic fields.
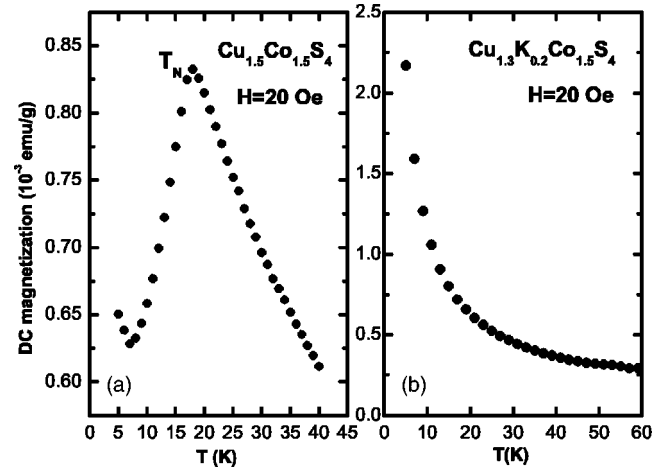

FIG. 7. Temperature dependence of magnetization, T_N is the Néel temperature.

surements, which is fully consistent with the diamagnetic measurement. Here midpoints of transition curve under different magnetic fields were selected as the criterion to define the upper critical field.

Above XRD pattern, EDAX of SEM, electrical resistivity and ac susceptibility indicate that the spinel Cu$_{1.3}$K$_{0.2}$Co$_{1.5}$S$_4$ we prepared is a superconductor with $T_c \approx 44$ K and a perfect Meissner fraction. We also prepared Cu$_{1.5}$Co$_{1.5}$S$_4$ and the T_c^{onset} is 4.0 K, which is consistent with the T_c of Cu$_{1.5}$Co$_{1.5}$S$_4$ reported by Furukawa *et al.*[8] The T_c between Cu$_{1.3}$K$_{0.2}$Co$_{1.5}$S$_4$ and Cu$_{1.5}$Co$_{1.5}$S$_4$ are so close that one cannot observe the effect of doping potassium. Thus, it is natural to question the effect of potassium for copper.

Furukawa *et al.* pointed out that Cu$_{1+x}$Co$_{2-x}$S$_4$ has a Curie-Weiss (CW) type susceptibility χ_{CW} with an antiferromagneticlike peak around 20 K, when x changes from 0 to 0.5, χ_{CW} becomes more prominent and T_c raises significantly from 0 to 4.0 K.[8] As to CuCo$_2$S$_4$, a piece of evidence for the S-wave superconductivity of an itinerant weak antiferromagnetism was also reported (with NMR).[12] So the relation between magnetism and superconductivity is the highlight to study the properties of thiospinel Cu$_{1+x}$Co$_{2-x}$S$_4$. Therefore it is necessary for us to observe the antiferromagnetism since only slight potassium substituted for copper based on Cu$_{1.5}$Co$_{1.5}$S$_4$.

Figure 7 shows the temperature dependence of dc magnetization measured at $H=20$ Oe for Cu$_{1.5}$Co$_{1.5}$S$_4$ and Cu$_{1.3}$K$_{0.2}$Co$_{1.5}$S$_4$, respectively. It is very clear that Cu$_{1.3}$K$_{0.2}$Co$_{1.5}$S$_4$ is of Curie type of paramagnetism, and no AF peak was observed from 9 K to 60 K, and Cu$_{1.5}$Co$_{1.5}$S$_4$ shows an AF behavior around 19 K, which is consistent with the report of Furukawa *et al.*[8] Thus, disappearance of AF provides extra evidence to distinguish Cu$_{1.3}$K$_{0.2}$Co$_{1.5}$S$_4$ from its parent phase Cu$_{1.5}$Co$_{1.5}$S$_4$. However one may argue that the disappearing of AF is caused by the decreasing Cu concentration, but weak antiferromagnetism of CuCo$_2$S$_4$ is also observed around 20 K,[8–10] so it is not possible for such an explanation. On the other hand, one may argue that the sample is not pure and another phase with paramagnetism prevails over the antiferromagnetism, but the magnitude of

paramagnetic $Cu_{1.3}K_{0.2}Co_{1.5}S_4$ is about 0.6×10^{-3} emu/g at 19 K as shown in Fig. 7(b), which is not big enough to smear the antiferromagnetism of $Cu_{1.5}Co_{1.5}S_4$ [the magnitude of antiferromagnetism is about 0.84×10^{-3} emu/g at 19 K as shown in Fig. 7(a)], so if the sample has two phases, the AF peak should also be observed in the dc magnetization of $Cu_{1.3}K_{0.2}Co_{1.5}S_4$, but no trace of AF peak is observed. Therefore this argument seems unlikely. On the contrary, this fact provides further evidence that the sample of $Cu_{1.3}K_{0.2}Co_{1.5}S_4$ is of single phase, which is different from its parent phase $Cu_{1.5}Co_{1.5}S_4$. Thus, a more reasonable picture would be that potassium substitution for Cu suppresses the weak antiferromagnetic order. We have also tried to fabricate the samples with different potassium concentration. It was found that when the nominal concentration of potassium is above 0.3, the sample is certainly not of single phase, while below 0.2, the sample is quite pure and a trend for the appearance of the AF peak is obvious towards less doping of potassium.

The almost unchanged T_c and destroyed AF behavior caused by potassium substitution for Cu could shed light on the properties of spinel materials $Cu_{1+x}Co_{2-x}S_4$ ($0 \leqslant x \leqslant 0.5$). $Cu_{1.5}Co_{1.5}S_4$ has a Curie-Weiss-type susceptibility with an AF peak around 20 K as shown in Fig. 7(a). When slight potassium is substituted for the copper, the AF peak disappears; this fact indicates that antiferromagnetism may stem from the copper ions. In the case of $Cu_{1.5}Co_{1.5}S_4$, Cu ions occupy not only the tetrahedral A site but also the octahedral B site based on the analysis of XRD patterns, so it is possible that the potassium atoms substituted for Cu occupy both A and B site. According to the NMR study, the Cu atoms substituted at the B site are in a nearly nonmagnetic state,[8] therefore the antiferromagnetism of $Cu_{1.5}Co_{1.5}S_4$ stems from the Cu atoms occupying the tetrahedral A site, when slight potassium atoms (as impurity) occupy A site; the antiferromagnetic spin correlation is destroyed.

When potassium atoms are substituted for copper atoms, T_c changes so little (the difference of T_c less than 0.4 K may be regarded as the fluctuation of superconducting transition temperature) and antiferromagnetism does not show up, this

may suggest that superconductivity has no direct relationship with antiferromagnetic spin correlation. This conclusion is in contrast with Furukawa's consideration, that the rise of T_c of $Cu_{1.5}Co_{1.5}S_4$ is strongly correlated with the growth of AF spin correlation.[8] According to this consideration, when copper concentration decreases from 1.5 to 1.3 stoichiometrically, the spin correlation is weakened and consequently superconducting transition temperature should decline. However, no decline of T_c is observed from our experiments. Wada *et al.*[10] studied the weak antiferromagnetism and superconductivity in spinel compounds $(Cu_xCo_{1-x})Co_2S_4$ by using NMR, and pointed out that the appearance of superconductivity for the compounds in the Cu-rich region ($x > 0.7$) is due to the large increase in $N(E_F)$ associated with Co atoms on the B site and the development of the AF spin correlation originates from the increase in $N(E_F)$ associated with Cu on the A site. Our results are consistent with Wada's conclusions. Therefore there is no direct relationship between superconductivity and AF correlation in the spinel materials $Cu_{1+x}Co_{2-x}S_4$.

IV. CONCLUSION

We succeeded in preparing spinel material $Cu_{1.3}K_{0.2}Co_{1.5}S_4$ with superconducting transition temperature of 4.2 K and no AF behavior is observed. It is concluded that the antiferromagnetism in spinel material $Cu_{1+x}Co_{2-x}S_4$ ($0 \leqslant x \leqslant 0.5$) may stem from the Cu atoms occupied on tetrahedral A site and no direct relationship between superconductivity and AF spin correlation is found.

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