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Weak antiferromagnetism and superconductivity in pseudo-binary spinel compounds $(\text{Cu},\text{Co})\text{Co}_2\text{S}_4$ investigated by ^{59}Co and ^{63}Cu magnetic resonance

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Abstract

We have carried out a nuclear magnetic resonance study on pseudo-binary spinel compounds $(\text{Cu}_x\text{Co}_{1-x})\text{Co}_2\text{S}_4$ with $x = 0-1.0$ to deduce the varied impact of variations in the antiferromagnetic (AF) spin correlation and density of states (DOS) that can clearly define the combination of magnetism and superconductivity in the system. The Curie–Weiss-type behaviour of the Knight shift K for both ^{59}Co and ^{63}Cu on the tetrahedral A site and the temperature-independent K for ^{59}Co on the octahedral B site indicate that the magnetism of the system originates from 3d bands associated with the transition-metal elements on the A site. With the Cu substitution x for Co on the A site, the negative Weiss temperature θ deduced from the K data initially decreases, takes a deep minimum around $x = 0.7$ followed by a rapid increase for $x \rightarrow 1$. For the compounds with $x \leq 0.3$ and $x > 0.8$, the nuclear spin–lattice relaxation rate T_1^{-1} for the nuclei on both A and B sites has a $T^{1/2}$ dependence at high temperatures, which is characteristic of three-dimensional itinerant weak antiferromagnets. In the Cu-rich region ($x > 0.7$) the compounds transform into a superconducting state below T_S with no long-range magnetic ordering. From a T_1^{-1} data analysis, we find that the increase of T_S correlates not only with the development of the AF spin correlation but also with the significant increase in the DOS at the Fermi level of the 3d bands $N_d(E_F)$ associated with Co on the B site. T_1^{-1} in the superconducting state of CuCo_2S_4 ($T_S = 4.4$ K), measured for ^{59}Co on the B site utilizing the pure quadrupole resonance spectrum, has a coherence peak followed by an exponential decrease, indicating that CuCo_2S_4 is an s-wave superconductor with an energy gap of $2\Delta = 4.14k_B T_S$. We conclude that the appearance of superconductivity for the compounds in the Cu-rich region originates from the large increase in $N_d(E_F)$ associated with Co

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on the B site, and the development of the AF spin correlation originates from the increase in $N_d(E_F)$ associated with Cu on the A site.

1. Introduction

Sulphospinel compounds AB_2S_4 (A and B = transition-metal elements) with metallic conductivity have been known to retain a large ionic character, which gives rise to a wide variety of physical phenomena such as magnetic ordering, superconductivity and metal–insulator transition. Among the compounds, we highlight the material $Cu_{1+y}Co_{2-y}S_4$ with a nominal Cu composition $y = 0–0.5$, which has aroused great interest due to the possible incidence of antiferromagnetism on the superconductivity [1,2]. The compounds have a Curie–Weiss-type susceptibility with a cusp around 18 K. The measurement of resistivity has shown a superconducting transition at T_S which depends on y , as is shown in the inset of figure 1. The nuclear magnetic resonance (NMR) investigation of $Cu_{1.5}Co_{1.5}S_4$ ($T_S = 2.3$ K) [3] has shown that the d hole band associated with Cu on the tetrahedral A site is mainly responsible for the spin paramagnetism. The nuclear spin–lattice relaxation rate T_1^{-1} for both ^{63}Cu on the A site and ^{59}Co on the octahedral B site has a $T^{1/2}$ dependence at high temperatures, which is expected for three-dimensional itinerant weak antiferromagnets. The Néel temperature for the staggered susceptibility has been estimated as $\simeq 19$ K. The greatest concern is the coexistence of the superconductivity and the weak antiferromagnetism in a newly synthesized $CuCo_2S_4$ with a higher transition temperature ($T_S = 4.4$ K) and an upper critical field ($H_{C2} \simeq 19$ kOe).

However, $CoCo_2S_4$ exhibits anomalous magnetic behaviour: a small peak around $\simeq 55$ K in the static susceptibility [4]; a small magnetic peak below 58 K in the neutron diffraction spectrum [5]; and the disappearance of the NMR signal of ^{59}Co on the A site below $\simeq 55$ K [6, 7]. These results suggest that $CoCo_2S_4$ transforms into an antiferromagnetic (AF)

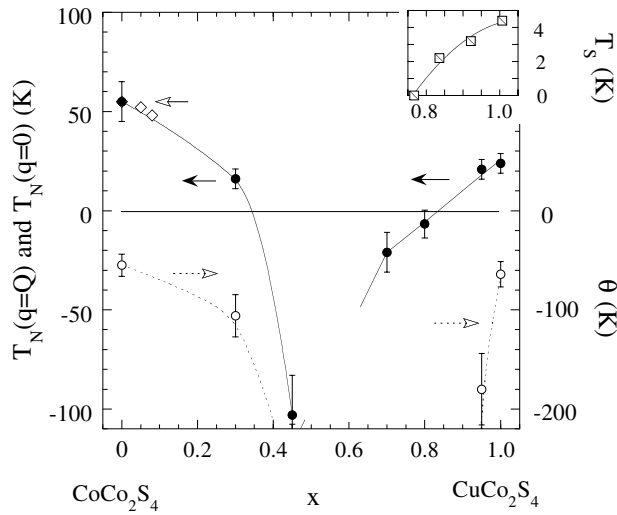


Figure 1. Weiss temperature θ (open circles), Néel temperature for the staggered susceptibility $T_N(q = Q)$ (closed circles), and Néel temperature of AF long-range ordering $T_N(q = 0)$ (open diamonds) plotted against Cu composition x . The inset shows the dependence of the superconducting transition temperature T_S on x .

long-range ordered state. Recently, Nishikawa *et al* [8] have found that a small substitution of Cu for Co on the A sites brings an anomalous increase in the magnetic resistivity below ~ 60 K.

In this paper, we report on the results of a systematic NMR investigation on pseudo-binary sulphospinel compounds (Cu_xCo_{1-x})Co₂S₄ with $x = 0-1.0$, which provide information on the varied impact of variations in the AF spin correlation and density of states (DOS) that can clearly define the combination of magnetism and superconductivity in this system. A more detailed account of the NMR data for Co-rich compounds ($x < 0.5$) and a preliminary experimental result for the CuCo₂S₄ compound have been published previously [7, 9].

2. Experiments

Polycrystalline samples of (Cu_xCo_{1-x})Co₂S₄, using $x = 0, 0.05, 0.08, 0.3, 0.5, 0.7, 0.8, 0.95$ and 1.0 in the present NMR study, were prepared by the standard vacuum ampoule method. The starting materials of CuS, CoS, Co and S were put in the ampoules, and were heated for 20 h at $500-800^\circ\text{C}$ depending on Cu composition. The samples were well synthesized only when ~ 2 wt% moisture was charged as a carrier gas. X-ray diffraction patterns at room temperature for the compounds with $x < 0.7$ are in good agreement with a single phase of the cubic spinel structure. The lattice constant a is plotted in figure 2 against nominal Cu composition y in Cu_{1+y}Co_{2-y}S₄. The nonlinear increase of a with y suggests a possible A–B site disorder for Cu heavy substitutions. The actual Cu composition x for the A site is given by the solid line in figure 2, which is estimated from the variation in ⁵⁹Co NMR intensities for the A site with y , as is described below. To synthesize the superconducting compounds close to CuCo₂S₄ ($x = 1.0$), a large amount of excess Cu atoms ($y = 0.5$) is required for the starting material. After synthesis, the excess of Cu atoms forms a small number of impurity phases: Cu₇S₄, Cu₉S₄ and Cu₉S₈, which were observed in the x-ray diffraction patterns as impurity lines.

With very careful sample preparation procedures, we can newly synthesize a stoichiometric CuCo₂S₄ compound, which has a rather high T_S of 4.4 K with a very sharp transition width ($\simeq 0.1$ K) and a perfect Meissner fraction.

The ⁵⁹Co (nuclear spin $I = 7/2$) and ⁶³Cu ($I = 3/2$) NMR measurements were carried out in a temperature range between 4.2–260 K with a phase-coherent spin–echo spectrometer operating at 75 MHz. The spin–echo NMR spectra were obtained in a field sweeping procedure. Nuclear spin–lattice relaxation times T_1 were measured utilizing a single radio frequency (rf) pulse saturation method.

We observed two distinct ⁵⁹Co NMR spectra [7]: an equally-split quadrupole powder-pattern spectrum which is assigned to the octahedral B sites with local trigonal crystal field; and a resonance line with a Lorentzian-like shape which is assigned to the tetrahedral A site with local cubic crystal field. These two spectra are labelled ⁵⁹Co[B] and ⁵⁹Co[A], respectively. The NMR intensity of ⁵⁹Co[A] at 4.2 K divided by that of ⁵⁹Co[B] is plotted in figure 3 against nominal Cu composition y . With increasing y , the ⁵⁹Co[A] NMR intensity decreases and approaches zero not at $y = 0$ but at 0.5. The NMR spectra of ⁶³Cu for most of the compounds with $y \geq 0$ also have a superposed structure of two distinct lines [3]: a large resonance line with a Lorentzian-like shape which is assigned to the A site; and a small broad line which is considered to be a quadrupolar broadened spectra on the B site. These lines are labelled ⁶³Cu[A] and ⁶³Cu[B], respectively. This gives evidence of a small amount of A–B site disorder for the Cu heavy substitutions.

Then, referring to the variation in the ⁵⁹Co[A] NMR intensity, we determine the actual Cu composition x given by the solid line in figure 3. The corresponding solid line in figure 2 reasonably gives an almost linear dependence of the lattice constant a on x . It is worth noting

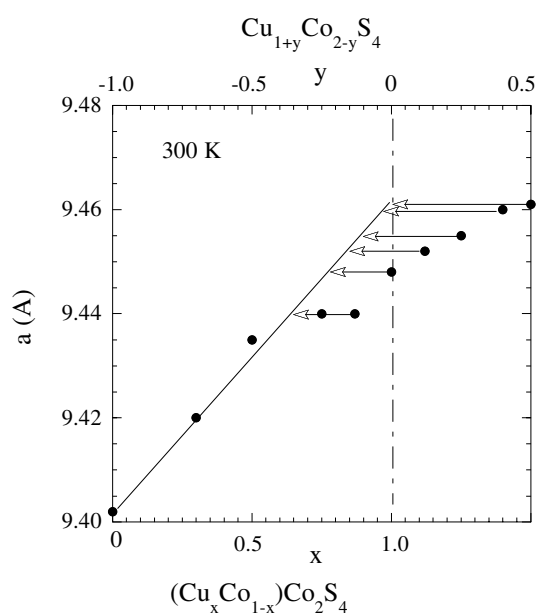


Figure 2. Plots of the lattice constant a against nominal Cu composition y in the notation of $\text{Cu}_{1+y}\text{Co}_{2-y}\text{S}_4$. The solid line gives the dependence of a on the actual Cu composition x in $(\text{Cu}_x\text{Co}_{1-x})\text{Co}_2\text{S}_4$ estimated from the ^{59}Co NMR intensity for the A site.

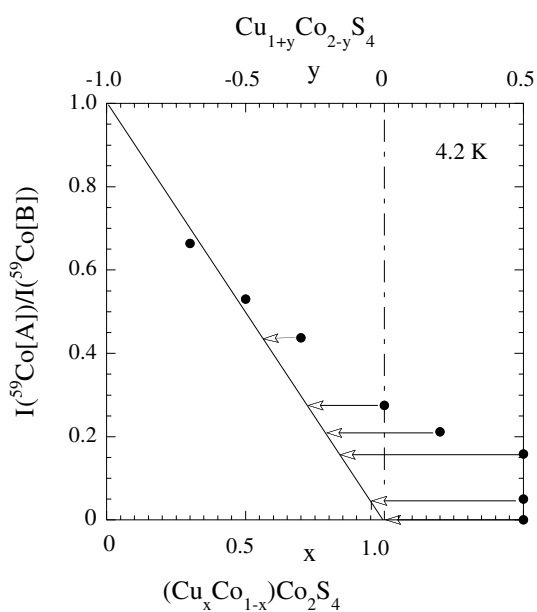


Figure 3. NMR intensity of ^{59}Co on the A site divided by that on the B site plotted against y . The solid line gives an estimate of the actual Cu composition x in $(\text{Cu}_x\text{Co}_{1-x})\text{Co}_2\text{S}_4$.

that, for the newly synthesized stoichiometric CuCo_2S_4 ($x = 1.0$), we do not find any sign of the site disorder in the NMR spectra.

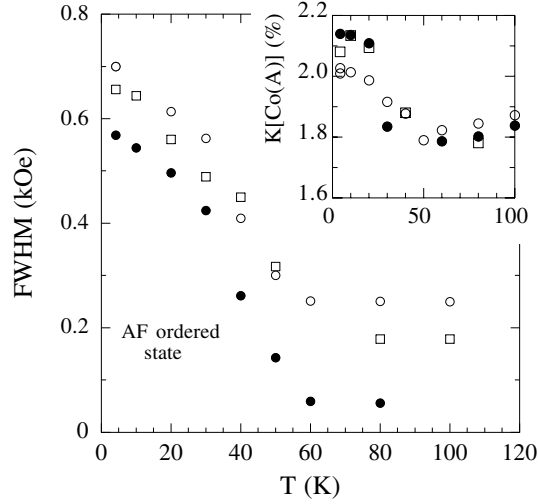


Figure 4. Temperature dependence of the linewidth of ^{59}Co on the A site for each of the compounds with $x = 0$ (closed circles), 0.05 (open squares) and 0.08 (open circles) at low temperatures. The inset shows the resonance shift tentatively determined at the peak intensity of the spectrum.

2.1. Knight shift

The NMR spectrum of $^{59}\text{Co}[\text{B}]$ with the quadrupole powder-pattern gives the values of the Knight shift $K(^{59}\text{Co}[\text{B}])$ and quadrupole frequency $\nu_Q(^{59}\text{Co}[\text{B}]) = e^2qQ/14\hbar$ as $\simeq 1.45\%$ and $\simeq 1.85$ MHz, respectively. Both $K(^{59}\text{Co}[\text{B}])$ and $\nu_Q(^{59}\text{Co}[\text{B}])$ are independent of both the temperature ($T = 4.2\text{--}260$ K) and the Cu substitution ($x = 0\text{--}1.0$).

The NMR spectrum of $^{59}\text{Co}[\text{A}]$ observed for the compounds with $x < 0.5$ has a Lorentzian-type lineshape at high temperatures, and shows a magnetic broadening at low temperatures. The temperature dependence of the Knight shift for $^{59}\text{Co}[\text{A}]$, $K(^{59}\text{Co}[\text{A}])$, determined at the peak intensity of the resonance line [7] can be reproduced with

$$K(T) = K_c + \frac{a}{T - \theta}. \quad (1)$$

The temperature-independent first term is estimated as $K_c \simeq 2.1\%$, which is independent of x . The x dependence of the Weiss temperature θ in the second term is shown in figure 1 by open circles. For CoCo_2S_4 , the value of $\theta = -55$ K deduced from the $K(^{59}\text{Co}[\text{A}])$ data significantly differs from -275 K estimated from the susceptibility data above 200 K [7]. This is probably due to a spurious contribution to the susceptibility even for $T > 200$ K from the extremely small amount of contaminated ferromagnet CoS_2 ($T_C = 124$ K).

For compounds with $x \leq 0.1$, we first succeeded in observing a largely broadened $^{59}\text{Co}[\text{A}]$ resonance spectrum for temperatures below $\simeq 55$ K with a prominent increase of the resonance shift, as shown in figure 4. This indicates that the compounds with $x \leq 0.1$ transform into an AF long-range ordered state below the Néel temperature $T_N(q = 0) \simeq 55$ K, where q is the wavenumber.

The NMR spectrum of ^{63}Cu on the A site for each of the compounds with $x \geq 0.7$ has a Lorentzian-like lineshape with almost temperature-independent linewidth. The Knight shifts for both $^{63}\text{Cu}[\text{A}]$ and $^{59}\text{Co}[\text{B}]$ in the compounds with $x = 0.95$ ($y = 0.5$) and $x = 1.0$ ($y = 0.5$) are plotted in figure 5 against temperature. As shown in the figure by solid curves, the $K(^{63}\text{Cu}[\text{A}])$ data can be reproduced satisfactorily by equation (1) with $K_c = 0.20\%$ and

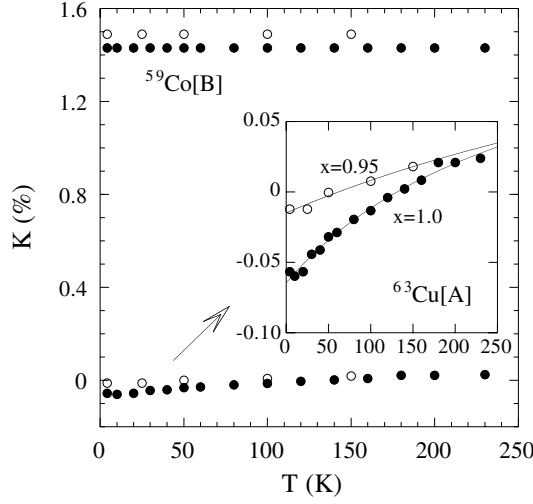


Figure 5. Knight shifts of ^{63}Cu on the A site and ^{59}Co on the B site for each of the compounds with $x = 0.95$ (open circles) and 1.0 (closed circles) plotted against temperature.

$\theta = -180$ K for $x = 0.95$, and $K_c = 0.15\%$ and $\theta = -64$ K for $x = 1.0$, respectively. The variation of the Weiss temperature θ with x is plotted in figure 1 by open circles. Though the χ data for the Cu-rich compounds exhibit a cusp around ~ 19 K [1], we do not find any sign of the AF long-range ordering in the NMR spectrum for either $^{63}\text{Cu}[\text{A}]$ or $^{59}\text{Co}[\text{B}]$.

2.2. Spin–lattice relaxation rate

The magnetization recovery curve $M(t)$ at a time t after the saturation rf pulse is given by [10, 11]

$$\frac{[M(\infty) - M(t)]}{M(\infty)} = a_1 e^{-b_1 t/T_1} + a_2 e^{-b_2 t/T_1} + a_3 e^{-b_3 t/T_1} + a_4 e^{-b_4 t/T_1} \quad (2)$$

where the coefficients b_i depend on the observed transition levels, and a_i depend on the initial saturation condition imposed on all spin levels. In the present initial condition of a single $\pi/2$ saturation pulse, b_i and a_i are given by $b_1 = 1$, $b_2 = 6$; $a_1 = 0.1$, $a_2 = 0.9$ for the central $|1/2\rangle \leftrightarrow |-1/2\rangle$ transition of ^{63}Cu NMR, and $b_1 = 1$, $b_2 = 6$, $b_3 = 15$, $b_4 = 28$; $a_1 = 0.013$, $a_2 = 0.068$, $a_3 = 0.206$, $a_4 = 0.714$ for the central transition of ^{59}Co NMR. The values of T_1 for both ^{59}Co and ^{63}Cu were determined by fitting the experimental $M(t)$ data with the theoretical recovery curve given by equation (2) with the corresponding parameters.

Figures 6 and 7 show the temperature dependence of $(T_1 T)^{-1}$ for both $^{59}\text{Co}[\text{A}]$ and $^{59}\text{Co}[\text{B}]$ in the compounds with $x = 0, 0.3$ and 0.5 and in the Cu-rich compounds with $x = 0.7$ ($y = 0$), $x = 0.8$ ($y = 0.2$), $x = 0.95$ ($y = 0.5$) and $x = 1.0$ ($y = 0.5$), respectively. In the paramagnetic state for both the Co-rich and Cu-rich compounds, $(T_1 T)^{-1}$ for both the A and B sites are significantly enhanced with the decreasing temperature. The $(T_1 T)^{-1}$ data at high temperatures can be reproduced by a sum of a temperature-independent relaxation term $(T_1 T)_c^{-1}$ and a temperature-dependent term $(T_1 T)_s^{-1}$ [12]

$$\frac{1}{T_1 T} = \frac{1}{(T_1 T)_c} + \frac{\beta}{\sqrt{T - T_N(q = Q)}} \quad (3)$$

as shown in the figures by solid curves, where Q is the AF number. The values of $T_N(q = Q)$ deduced from the temperature-dependent second term are plotted in figure 1 against x as closed

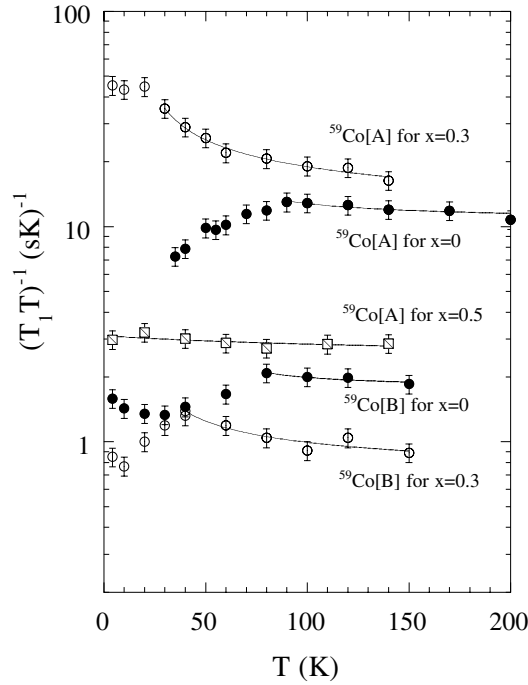


Figure 6. Temperature dependence of $(T_1 T)^{-1}$ of ^{59}Co on the A and B sites for each of the Co-rich compounds with $x = 0, 0.3$ and 0.5 .

circles. Figure 8 shows the x dependence of the first temperature-independent term for both A (open symbols) and B (closed symbols) sites.

For the superconducting CuCo_2S_4 ($T_S = 4.4$ K), T_1^{-1} of ^{59}Co on the B sites was also measured in zero field utilizing the pure quadrupole resonance around 5.6 MHz, which corresponds to the $|\pm 7/2\rangle \leftrightarrow |\pm 5/2\rangle$ transition separated in frequency by $3\nu_Q$. The recovery behaviour of the magnetization after the $\pi/2$ saturation pulse can be reproduced by equation (2) with $b_1 = 3$, $b_2 = 10$, $b_3 = 21$, and $a_1 = 0.214$, $a_2 = 0.649$, $a_3 = 0.136$. The values of T_1 in the temperature range between 1.4 and 50 K are plotted in figure 9 against the inverse of the reduced temperature T_S/T . T_1^{-1} in the superconducting state exhibits a coherence peak just below T_S followed by an exponential decrease.

3. Discussion

The strong crystal electric field (CEF) theory leads the sulphospinel compounds to the $A^{2+}(B^{3+})_2(S^{2-})_4$ ionic state: the ground-state electron configuration is $(e_g)^4(t_{2g})^3$ (spin $S = 3/2$) for Co[A], $(e_g)^4(t_{2g})^5$ ($S = 1/2$) for Cu[A], and $(t_{2g})^6$ ($S = 0$) for Co[B], respectively. The full-potential linearized augmented plane wave (LAPW) band calculation for CuCo_2S_4 by Oda *et al* [13] has shown that the electronic states near the Fermi level E_F consist mainly of the Co 3d and the S 3p orbitals. The Cu 3d orbitals form relatively narrow bands and are almost completely occupied by electrons, which leads the valence of Cu[A] to the nonmagnetic Cu^{1+} rather than the magnetic Cu^{2+} . However, the LAPW band calculation for CoCo_2S_4 by Miyazaki *et al* [14] has shown that the 3d component of Co[A] is dominant in the DOS at E_F .

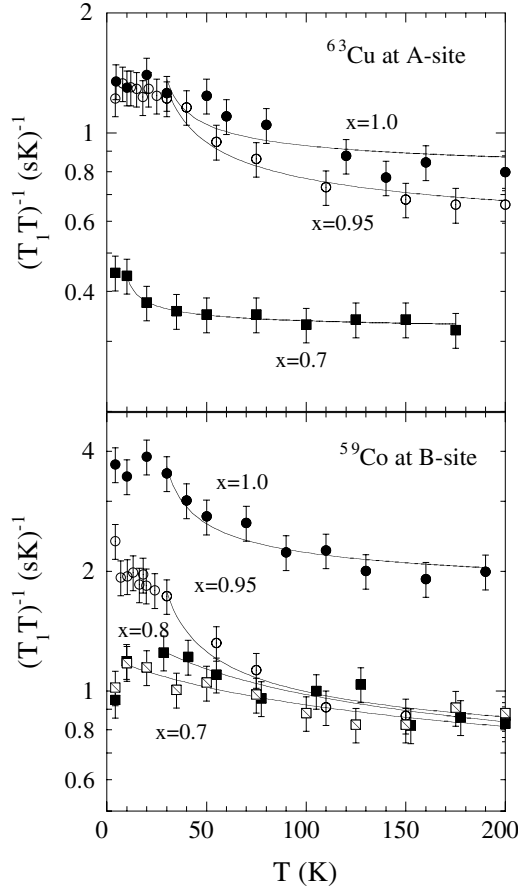


Figure 7. Temperature dependence of $(T_1T)^{-1}$ of ^{63}Cu on the A site and ^{59}Co on the B site for each of the compounds with $x = 0.7, 0.8, 0.95$ and 1.0 .

The Knight shift K is a measure of the uniform susceptibility $\chi(0, 0)$. The temperature-independent behaviour of $K(^{59}\text{Co}[\text{B}])$ for all the compounds ($x = 0-1.0$) is consistent with the nonmagnetic electronic state of $\text{Co}[\text{B}]$ expected from the strong CEF scheme. The large positive value of $K(^{59}\text{Co}[\text{B}])$, 1.45%, is indicative of a dominant d orbital contribution. In contrast, for both $^{59}\text{Co}[\text{A}]$ in the Co-rich compounds and $^{63}\text{Cu}[\text{A}]$ in the Cu-rich compounds, K has a Curie–Weiss-type behaviour, indicating that the 3d bands associated with the transition-metal elements on the A site carry the magnetic moment. With the increase of the Cu composition x , as shown in figure 1 by open circles, the negative Weiss temperature θ initially decreases, and takes a deep minimum around $x = 0.7$ followed by a rapid increase for $x \rightarrow 1$. The magnetic behaviour of $K(^{63}\text{Cu}[\text{A}])$ for the Cu-rich compounds is consistent with the Cu^{2+} ionic state expected from the strong CEF scheme, rather than the Cu^{1+} state predicted by the LAPW band calculation.

The Co-rich compounds with $x = 0, 0.05$ and 0.08 exhibit AF long-range ordering below $T_N(q = 0) \simeq 55$ K, which is evidenced by the prominent linewidth broadening of the ^{59}Co resonance spectrum on the A site. The linewidth ΔH in the AF ordered state is given by the spin hyperfine field $H_{\text{hf}}(s)$ and the effective moment μ_{eff} as

$$\Delta H \sim \mu_{\text{eff}} H_{\text{hf}}(s). \quad (4)$$

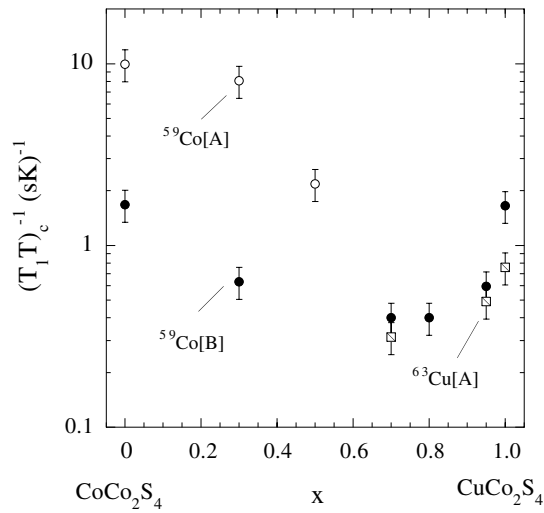


Figure 8. Temperature-independent relaxation term $(T_1 T_c)^{-1}$ for both A and B sites plotted against x .

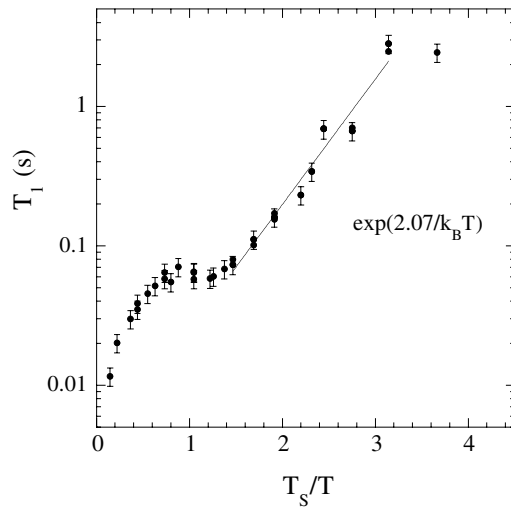


Figure 9. T_1 of ⁵⁹Co on the B site of CuCo₂S₄ ($T_S = 4.4$ K) in zero field plotted against the inverse of the reduced temperature T_S/T .

Taking the experimental value of $H_{\text{hf}}(s) \simeq -26 \text{ kOe}/\mu_B$ for Co[A] [7], $\Delta H \simeq 0.6 \text{ kOe}$ at 4.2 K gives a very small μ_{eff} of about $0.023 \mu_B$. The anomalous increase in the magnetic resistivity observed below ~ 60 K for the compounds with $0.01 < x < 0.1$ [8] can be ascribed to the AF long-range ordering: the Cu light substitution for Co on the A sites is considered to disturb the AF ordered spin waves and gives scattering centres which cause the increase in the magnetic resistivity.

The nuclear spin-lattice relaxation rate T_1^{-1} is a measure of fluctuations of the internal field, and the second spin term $(T_1 T_s)^{-1}$ in equation (3) provides information on the q -sum of

the low-frequency dynamical susceptibility $\chi(q, \omega)$

$$\frac{1}{(T_1 T)_s} = \frac{\gamma_n^2 k_B}{2\mu_B^2} \sum_q \frac{A_{\text{hf}}^2 \text{Im}\chi(q, \omega_0)}{\omega_0} \quad (5)$$

in contrast to the d spin part of the Knight shift that is proportional to $\chi(0, 0)$. Here, $A_{\text{hf}} = \gamma_n \hbar H_{\text{hf}}(s)/S(S+1)$ and ω_0 is the NMR frequency. The self-consistent renormalization theory for the three-dimensional weak antiferromagnets [12] predicts the $T^{1/2}$ dependence of T_1^{-1} for $T \gg T_N(q=Q)$, where $T_N(q=Q)$ is the Néel temperature for the staggered susceptibility $\chi(Q, \omega)$. The temperature-dependent behaviour of $(T_1 T)_s^{-1}$ for both the A and B sites is considered to be mainly attributed to $\chi(Q, \omega)$, since $K(^{59}\text{Co}[\text{B}])$ is independent of temperature.

The variation of $T_N(q=Q)$ with the Cu composition x is shown in figure 1 by closed circles. The positive $T_N(q=Q)$ for $x \leq 0.3$ and $x > 0.8$ and the negative $T_N(q=Q)$ for $0.3 < x \leq 0.8$ indicate that the compounds belong to a group of weak antiferromagnets and nearly antiferromagnets, respectively. The decrease in the AF spin correlations for the compounds with $0.3 < x \leq 0.8$ is considered to be caused by the random distribution of Cu and Co atoms on the A sites.

The temperature-independent first term in equation (3) arises mainly from the orbital relaxation process to the conduction electrons given by [15]

$$\frac{1}{(T_1 T)_{\text{orb}}} = 4\pi \gamma_n^2 \hbar k_B H_{\text{hf}}(\text{orb})^2 N_d(E_F)^2 p \quad (6)$$

where $H_{\text{hf}}(\text{orb}) = 2\mu_B k \langle r^{-3} \rangle_d$ is the orbital hyperfine field, k is the reduction factor in metals, and $N_d(E_F)$ is the DOS at E_F of the 3d bands. As $H_{\text{hf}}(s) \ll H_{\text{hf}}(\text{orb})$ in this system [3, 7], the relaxation process to the conduction electrons through the core polarization hyperfine coupling gives a negligible contribution to the experimental $(T_1 T)_c^{-1}$.

In equation (6) p is the reduction factor that depends on the relative weight at E_F of the irreducible representation of the atomic d functions. For the cubic point group

$$p = \frac{2}{3} f(\Gamma_5) \left\{ 2 - \frac{5}{3} f(\Gamma_5) \right\} \quad (7)$$

where $f(\Gamma_5)$ is the relative weight of the Γ_5 representation at E_F . Using $\langle 1/r^3 \rangle_d = 6.04, 6.70$ and 8.25 au for $\text{Co}^{2+}, \text{Co}^{3+}$ and Cu^{2+} ([16]), and $k = 0.8$, equation (6) yields values of $N_d(E_F)$ for the corresponding 3d bands. Here, the value of p is taken to be $2/9$, because the Γ_5 representation is considered to dominate at E_F : $f(\Gamma_5) \simeq 1$ for each of the 3d bands [13, 14]. The variations of $N_d(E_F)$ with x for $\text{Co}[\text{A}], \text{Cu}[\text{A}]$ and $\text{Co}[\text{B}]$ are plotted in figure 10. The dominant contribution to $N_d(E_F)$ for CoCo_2S_4 is from the 3d component of $\text{Co}[\text{A}]$, and for CuCo_2S_4 from that of $\text{Co}[\text{B}]$, consistent with the corresponding theoretically calculated band structures [13, 14].

We are now concerned with the superconductivity observed for the compounds in the Cu-rich region. As can be seen in figure 1, the increase in the superconducting transition temperature T_S correlates with the development of AF spin correlations, which suggest a possible d-wave symmetry of the superconducting electron-pair wavefunction, as in some of the heavy Fermion superconductors [17] and the high- T_S Cu oxide superconductors [18]. In addition, we have found that the increase in T_S also correlates with the increase in $N_d(E_F)$ for the B site, which suggests an s-wave symmetry for BCS superconductors [19]. The measurement of T_1^{-1} in the superconducting state has been known to be useful to envisage the symmetry of the superconducting wavefunction: the T^n dependence for the non s-wave symmetry; and the coherence peak followed by exponential decrease for the s-wave symmetry. As is shown in figure 9, the experimental T_1^{-1} for $^{59}\text{Co}[\text{B}]$ in the superconducting state clearly exhibits the coherence peak just below T_S and decreases exponentially at lower temperatures. The

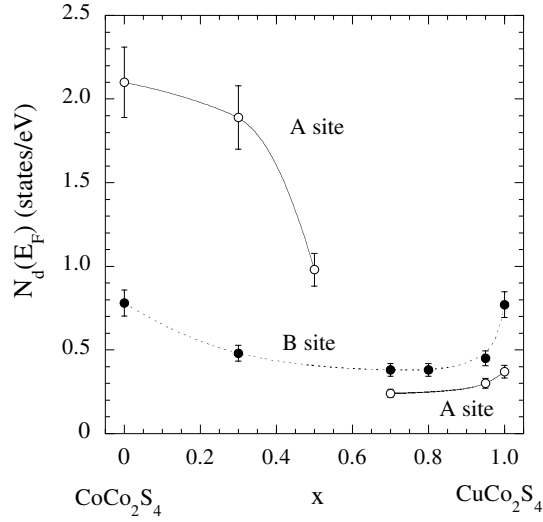


Figure 10. DOS of 3d bands at the Fermi level for both A and B sites, estimated from $(T_1 T_c)^{-1}$ data through the procedures described in the text.

slope of $\ln T_1$ versus T_S/T plots at $T \ll T_S$ gives a rather large superconducting energy gap of $2\Delta = 4.14k_B T_S$. This is an indication that CuCo₂S₄ is a strongly phonon-coupled s-wave superconductor. Then, we may conclude that the appearance of the superconductivity for the compounds in the Cu-rich region originates from the large increase in the DOS of the 3d bands associated with Co on the B site, and that the development of the AF spin correlation originates from the increase in the DOS of the 3d bands associated with Cu on the A site.

4. Conclusion

The electronic and magnetic properties of pseudo-binary spinel compounds $(\text{Cu}_x\text{Co}_{1-x})\text{Co}_2\text{S}_4$ ($x = 0-1.0$) have been investigated with the ⁵⁹Co and ⁶³Cu magnetic resonance measurements. The Curie–Weiss-type behaviour of K for nuclei on the tetrahedral A site indicates that the magnetism of the system originates from the 3d bands associated with the transition-metal elements on the A site. With the Cu substitution x for Co on the A site, the negative Weiss temperature θ deduced from the K data initially decreases, takes a deep minimum around $x = 0.7$ followed by a rapid increase for $x \rightarrow 1$. For the compounds with $x \leq 0.3$ and $x > 0.8$, T_1^{-1} for both the A and B sites has a $T^{1/2}$ dependence at high temperatures, which is a characteristic of three-dimensional itinerant weak antiferromagnets. In the Co-rich region ($x < 0.1$), the compounds exhibit an AF long-range ordering below $\simeq 55$ K with a very small effective moment of $0.023 \mu_B$. In the Cu-rich region ($x > 0.7$), however, the compounds transform into a superconducting state with no long-range magnetic ordering. T_1^{-1} of ⁵⁹Co on the B site measured in the superconducting state of CuCo₂S₄ ($T_S = 4.4$ K) has a coherence peak followed by exponential decrease, indicating that CuCo₂S₄ is an s-wave superconductor with the energy gap of $2\Delta = 4.14k_B T_S$. It is concluded that the appearance of the superconductivity for the compounds in the Cu-rich region originates from the large increase in the DOS at E_F of the 3d bands associated with Co on the B site, and the development of the AF spin correlation originates from the increase in the DOS of the 3d bands associated with Cu on the A site.

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