Structure and Magnetic Properties of Quasi-One Dimensional Cobalt-Doped Scandium Cuprate Compounds

Nobuhito IMANAKA, Toshihiro SHIMIZU, Fumihiko SAITO, Yasuyuki KOBAYASHI,
Gin-ya ADACHI, Guo LIU* and John Edward GREEDAN*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1, Yamadaoka, Suita-shi, Osaka 565

*Institute for Materials Research, McMaster University, 1280, Main Street West, Hamilton, Ontario L8S 4M1, Canada

コバルトを添加した、擬一次元的配列を持つスカンジウム銅化合物の構造と磁気的性質

今中信人・清水敏宏・斎藤文彦・小林靖之・足立吟也・Guo Liu・John Edward Greedan

大阪大学工学部応用化学科, 565 吹田市山田丘 2-1

*Institute for Materials Research, McMaster University, 1280, Main Street West, Hamilton, Ontario L8S 4M1, Canada

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Structure and magnetic properties of the $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$ system were investigated up to the solid solution limits $x=0.4$ and $x=0.6$. Undoped $\text{Sc}_2\text{Cu}_2\text{O}_5$ has, like isostructural $\text{Y}_2\text{Cu}_2\text{O}_5$, a magnetic structure with weak ferromagnetic coupling along the b -axis and strongly coupled Cu^{2+} chains parallel to the a -axis which were antiferromagnetically coupled below the Néel temperature of 16 K. Doping with Co^{2+} caused the paramagnetic Curie temperature (θ_p) to decrease from the $x=0$ value of 40 K, making (θ_p) negative for $x>0.2$, and caused the Néel temperature to increase to about 35 K for $x=0.4$. Thus the interchain weak ferromagnetic coupling along the b -axis was weakened and the interchain antiferromagnetic coupling was strengthened, while the intrachain strong ferromagnetic coupling, which displays the one-dimensional spin-spin interaction, was not influenced by the Co doping. Room-temperature structure refinement for $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$ from neutron powder diffraction data indicated that random substitution of Co^{2+} for Cu^{2+} occurred and that the Cu-O-O-Cu interchain superexchange pathway was enhanced by geometric changes as x increased from $x=0$ to 0.4.

Key-words: Cuprate, Scandium, Ferromagnetism, Antiferromagnetism, Superexchange, Néel temperature, Spin-spin interaction

1. Introduction

Rare earths such as Tb-Lu, Y and Sc, have been found to form the oxide $\text{Ln}_2\text{Cu}_2\text{O}_5$ (225) (Ln =rare earths), which is isostructural with $\text{Ho}_2\text{Cu}_2\text{O}_5$.^{(1),(2)} Among this $\text{Ln}_2\text{Cu}_2\text{O}_5$ series, the magnetic properties of $\text{Y}_2\text{Cu}_2\text{O}_5$ have been investigated in detail,⁽³⁾⁻¹¹⁾ since the $\text{Y}_2\text{Cu}_2\text{O}_5$ phase was found as one of the contaminant in the preparation of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (123) superconductor. In addition, the 123 oxide itself shows antiferromagnetic order for $\delta>0.6$.⁽¹²⁾ Cuprate compounds containing rare earths have received considerable attention due to their interesting magnetic properties as well as their superconducting characteristics.

In the $\text{Ln}_2\text{Cu}_2\text{O}_5$ structure, Cu and O form chains of square planer units which alternatively share corners and edges parallel to the a -axis,⁽⁴⁾ and Cu^{2+} in these chains strongly orders ferromagnetically and causes the one-dimensional magnetic characteristics. Another weak ferromagnetic coupling also exists along the b -axis in the 225 compounds. The $\text{Y}_2\text{Cu}_2\text{O}_5$ phase shows an antiferromagnetic-paramagnetic transition at around 13 K. Below the Néel temperature (T_N), antiferromagnetic ordering appears in the c -axis direction. A scandium ion, whose ionic radius is the smallest among the rare earths, also retains the same $\text{Ho}_2\text{Cu}_2\text{O}_5$ structure. Since the ionic radius of Sc is smaller than that of Y, the interchain coupling is strengthened. This causes the enhancement of the Néel temperature (T_N values for $\text{Sc}_2\text{Cu}_2\text{O}_5$ and $\text{Y}_2\text{Cu}_2\text{O}_5$ are 16 K⁽⁴⁾ and 13 K,⁽⁵⁾ respectively). For the purpose of obtaining distinct characteristics of magnetic behavior through the intra- and interchain coupling of Cu-O chains in the 225 compounds, $\text{Sc}_2\text{Cu}_2\text{O}_5$ is the most appropriate candidate for investigation in the $\text{Ln}_2\text{Cu}_2\text{O}_5$ series. Some magnetic properties^{(4),(7)-(10),(14)} have been elucidated for $\text{Sc}_2\text{Cu}_2\text{O}_5$ in order to clarify the magnetic behavior of pure $\text{Sc}_2\text{Cu}_2\text{O}_5$, in addition to the vibrational spectra and electrical properties,⁽¹³⁾ and neutron diffraction analyses have also been performed.^{(9),(14)}

In this study, another magnetic ion, Co^{2+} (high spin: 0.0885 nm, low spin: 0.079 nm),⁽¹⁵⁾ whose ionic radius is similar to both Sc^{3+} (0.0885 nm)⁽¹⁵⁾ and Cu^{2+} (0.087 nm),⁽¹⁵⁾ was doped in $\text{Sc}_2\text{Cu}_2\text{O}_5$ to form a solid solution to investigate the magnetic properties in more detail. The influence of Co^{2+} incorporation on the 225 structure and magnetic properties was investigated.

2. Experimental

Appropriate amounts of Sc_2O_3 (purity: 99.9%), CuO (purity: 99.99%), and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (reagent grade) were weighed, mixed in an agate mortar and then pelletized. The pellets were heated at 1000°C

Fig. 1. Variations of the lattice parameter a (I) and the lattice parameters b and c (II) as functions of Co content (x) in $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$.

for 6h in a flowing oxygen atmosphere and then cooled in the furnace. Since the ionic radius of Co^{2+} is similar to those of Sc^{3+} and Cu^{2+} , two types of mixtures were prepared. Type I assumes Co substitution for Cu, i.e., $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$, and Type II assumes Co substitution for Sc, i.e., $\text{Sc}_2\text{Cu}_x\text{Co}_{2-x}\text{O}_{5-x/2}$. X-ray powder diffraction data were obtained using a diffractometer (Rotaflex) from Rigaku Corporation. Lattice parameters were refined using high-resolution Guinier camera data with $\text{Cu K}\alpha_1$ radiation and a Si standard. Magnetic susceptibility measurements were performed using a torsion magnetic balance from 4.2 to 300 K at an applied magnetic field of 0.6 T. Neutron diffraction data were obtained by means of the McMaster Nuclear Reactor at McMaster University, Ontario, Canada, using a 0.13913 nm neutron beam obtained by reflection from a $\text{Cu}(200)$ monochromator. Details of the refinement methods have been described previously.¹⁶⁾ Neutron scattering length (fm) used were 12.29, 2.50, 7.718, 5.803 for Sc, Co, Cu and O, respectively.¹⁷⁾ The atomic ratio of Sc, Cu and Co was determined by an X-ray fluorescence analyzer, System 3270A from Rigaku Corporation. The oxygen content was measured by an oxygen analyzer, MGA-650 from Horiba Ltd.

3. Results and discussion

On the basis of charge considerations, Co^{2+} is most likely to substitute for Cu^{2+} ; however, it is not possible to rule out, a priori, Co^{2+} substitution for Sc^{3+} . Thus, two solid solution series were investigated initially, namely $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$ (Type I) and $\text{Sc}_{2-x}\text{Co}_x\text{Cu}_2\text{O}_{5-x/2}$ (Type II). A single-phase material, isostructural with $\text{Sc}_2\text{Cu}_2\text{O}_5$, was obtained by Co substitution from $x=0.2$ to up to 0.4 in $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$ (Type I). For $x=0.6$, a few peaks belonging to Sc_2O_3 and Co_3O_4 were observed in addition to the peaks identified as belonging to the $\text{Sc}_2\text{Cu}_2\text{O}_5$ structure. In the series of X-ray measurements for the Sc-Cu-Co-O solid solutions, some peaks corresponding to the $\text{Sc}_2\text{Cu}_2\text{O}_5$ structure monotonically shifted with the increase in Co substitution. On the other hand, in the case of Type II, CuO was observed in all the samples prepared. Co_3O_4 peaks

also existed in the samples of $\text{Sc}_{2-x}\text{Co}_x\text{Cu}_2\text{O}_{5-x/2}$ from $x=0.2$ to 0.6. From these results, we can conclude that the Co substitutes not for the Sc site but for the Cu site and forms a solid solution, up to $x=0.4$ in Type I ($\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$). From the X-ray fluorescence and oxygen content analyses, the atomic ratio in the solid solutions was found to be almost the same as that in the nominal composition $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$.

Figures 1 (I) and (II) show how the lattice parameters a , b and c axes change with the amount of Co substitution in $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$. The lattice parameter c monotonically increased up to $x=0.4$. In contrast, lattice parameter b decreased up to the same level of Co substitution. No clear deviation was found in lattice parameter a in the range of compositions studied here. These results indicate that the Co solubility limit in $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$ is around $x=0.4$.

Figure 2 presents the temperature dependence (4.2–300 K) of the magnetic susceptibilities of $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$ ($x=0-0.6$). In order to clarify the difference in the magnetic properties resulting from the Co substitution, $1/\chi_m - T$ (4.2–300 K) relationships for $\text{Sc}_2\text{Cu}_2\text{O}_5$ (without Co substitution) and $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$ (maximum Co substitution) are shown in Fig. 3. $\text{Sc}_2\text{Cu}_2\text{O}_5$ has already been reported to transform from paramagnetic to antiferromagnetic at around 16 K with decreasing temperature.⁴⁾ The Néel temperature (T_N) obtained in our experi-

Fig. 2. Temperature dependence of the magnetic susceptibilities of $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$ ($x=0$ (○), $x=0.2$ (●), $x=0.4$ (◇), and $x=0.6$ (▲)).

Fig. 3. The $1/\chi_m$ - T relationships for $\text{Sc}_2\text{Cu}_2\text{O}_5$ (○) and $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$ (●).

Fig. 4. Relationship between T_N and the amount of Co substitution in $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$.

ment for $\text{Sc}_2\text{Cu}_2\text{O}_5$ ($x=0$) is almost consistent with this reported temperature. In the temperature region lower than T_N , the magnetic susceptibility decreased. This is mainly attributed to the decrease in the magnetic moment, which due to results from random ordering by thermal vibration and reduces the magnetic moment which would be magnetized by the external field. At higher temperatures, the $1/\chi_m$ - T relationship was almost linear and obeyed the Curie-Weiss law.

Figure 4 presents the relationship between T_N and the amount of Co substitution in $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$. T_N increased linearly up to $x=0.4$. This is the same behavior as that of the lattice parameter c variation with Co substitution as shown in Fig. 1(II). This increase in T_N occurred as a result of the substitution of Cu sites by Co to form a solid solution of $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$.

Figure 5 shows the $\text{Ho}_2\text{Cu}_2\text{O}_5$ -type structure in the ac plane, which has been already reported.⁹⁾ ⊕ and ⊖ indicate the spins of Cu ions when Cu between the chains (along the c -axis) orders antiferromagnetically. Cu^{2+} is wellknown to form a square planar coordination. However, in the case of $\text{Sc}_2\text{Cu}_2\text{O}_5$, six oxygen atoms coordinate to a Cu^{2+} ion to form an octahedron and these six oxygen atoms are highly distorted. That is, the two axial oxygen atoms are longer than the four equatorial ones. Therefore, $d_{x^2-y^2}$ orbitals in Cu are half-filled and d_{z^2} orbitals are com-

Fig. 5. Illustration of $\text{Ho}_2\text{Cu}_2\text{O}_5$ structure in the ac plane without Ho ions. Spin orientations of Cu^{2+} in the antiferromagnetic state are indicated by symbols ⊕ and ⊖.

pletely filled. The isolated spin in the $d_{x^2-y^2}$ orbital of every Cu ion in the Cu-O chain (a -axis) is strongly ordered ferromagnetically by the super-exchange with the combination of oxygen p orbitals and shows one-dimensional interaction characteristics along the a -axis. In addition to this, weak ferromagnetic interaction exists between the a -axis along the b -axis.⁹⁾ Along the c -axis, the isolated spin in Cu^{2+} weakly orders antiferromagnetically.

In the neutron diffraction refinement for $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$, three models have been postulated. The first one is that Co ions substitute only for Cu_1 sites in Fig. 5. The second is that Co ions substitute only for Cu_2 sites. The third is that doped Co ions equally substitute for both Cu_1 and Cu_2 sites. Although all three models can be refined to the same degree, the first two models gave negative individual temperature factors for the Cu and Co atoms. The third (disordered-Co) model gave realistic temperature factors for all atoms. Based on the neutron refinement results, we can conclude that the third model, where Co equally substitutes for both Cu_1 and Cu_2 sites, is most appropriate. The results of the refinement are listed in Table 1 and bond distances and bond angles are tabulated in Table 2. From the refinement results, the $\text{Cu}_1\text{-O}_4$ and $\text{O}_5\text{-Cu}_1$ angle in the $\text{Cu}_1\text{-O}_4\text{-O}_5\text{-Cu}_1$ ordering illustrated in Fig. 6 is calculated to be 130.4° and 135.5° for $\text{Sc}_2\text{Cu}_2\text{O}_5$ and $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$, respectively. In the case that Co^{2+} partially substitutes for the Cu site in the $\text{Sc}_2\text{Cu}_2\text{O}_5$ structure, the lattice parameter c increases as shown in Fig. 1(II). However, the distance between O_4 and O_5 was found to decrease from 0.294 to 0.285 nm by the neutron refinement. This means that the Cu-O-O-Cu ordering along the c -axis approaches a more

Table 1. Crystallographic Parameters of $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$ from Neutron Powder Diffraction Data

Space Group:		Pna2 ₁				
Unit Cell Parameters (nm):		a=1.0427(2) b=0.32112(5) c=1.2069(2) Z=4				
Atom	Site	x	y	z	B(nm ²)	Occupancy
Sc1	4a	0.217(1)	0.223(4)	0.0	0.006(3)	1.0
Sc2	4a	0.041(1)	0.225(3)	0.3318(6)	0.004(3)	1.0
Cu1/Co2	4a	0.992(3)	0.866(8)	0.109(3)	0.002(4)	0.8/0.2
Cu2/Co2	4a	0.254(3)	0.672(7)	0.219(3)	0.009(4)	0.8/0.2
O1	4a	0.170(2)	0.727(2)	0.357(2)	0.002(1)	1.0
O2	4a	0.327(2)	0.720(8)	0.068(3)	0.002(1)	1.0
O3	4a	0.124(5)	0.282(7)	0.172(3)	0.002(1)	1.0
O4	4a	0.437(3)	0.769(9)	0.268(3)	0.002(1)	1.0
O5	4a	0.415(3)	0.253(8)	0.459(2)	0.002(1)	1.0
Nuclear R _w				0.0490		
Profile R _p				0.0379		
Weighted Profile R _{wp}				0.0504		
Expected R _e				0.0294		
No. of Profile Points N				961		
No. of Parameters Refined				47		
No. of Independent Reflections				351		
2 θ Range (°)				12-108		

Table 2. Bond Distances (nm) and Bond Angles (°) in $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$

Sc1-O1	0.209(3)	Sc2-O1	0.212(3)
Sc1-O2	0.213(3)	Sc2-O3	0.212(4)
Sc1-O2'	0.214(3)	Sc2-O4	0.210(3)
Sc1-O3	0.230(4)	Sc2-O4'	0.207(3)
Sc1-O5	0.224(3)	Sc2-O5	0.202(3)
Sc1-O5'	0.210(3)	Mean	0.209
Mean	0.217		
Cu1/Co1-O2	0.183(4)	Cu2/Co2-O1	0.189(4)
Cu1/Co1-O3	0.199(5)	Cu2/Co2-O2	0.198(4)
Cu1/Co1-O4	0.201(5)	Cu2/Co2-O3	0.193(5)
Cu1/Co1-O5	0.207(4)	Cu2/Co2-O4	0.202(4)
Mean	0.198	Mean	0.196
Cu1/Co1-Cu2/Co2		0.303(4)	
Cu1/Co1-Cu2/Co2		0.286(4)	
O2-Cu1/Co1-O3	151(2)	O1-Cu2/Co2-O2	169(2)
O2-Cu1/Co1-O4	88(2)	O1-Cu2/Co2-O3	90(2)
O2-Cu1/Co1-O5	100(2)	O1-Cu2/Co2-O4	99(2)
O3-Cu1/Co1-O4	84(2)	O2-Cu2/Co2-O3	93(2)
O3-Cu1/Co1-O5	96(2)	O2-Cu2/Co2-O4	84(2)
O4-Cu1/Co1-O5	162(2)	O3-Cu2/Co2-O4	148(2)

linear configuration and that distance between oxygen atoms O₄ and O₅ decreases due to the Co doping. As a result, the overlap between two p orbitals of the O atoms in the Cu-O-O-Cu arrangement increases as shown in Fig. 6.

Another Cu-O-O-Cu arrangement also appears in Cu₂-O₁-O₂-Cu₂ (Fig. 5). However, in this case, the distance between the two oxygen atoms for $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$ is 0.302 nm, which is 0.008 nm longer than that for $\text{Sc}_2\text{Cu}_2\text{O}_5$. In addition, the direction of the Cu₁ to O₄ and Cu₁ to O₅ vector is in a cross direction, while that of Cu₂ to O₁ and Cu₂ to O₂ one is rather a parallel one. Therefore, the spin-spin inter-

Fig. 6. Schematic representation of the overlap between p orbitals in two oxygen atoms for the Cu₁-O₄-O₅-Cu₁ arrangement.

action between the p orbitals of two oxygen atoms is expected to occur mainly in the Cu₁-O₄-O₅-Cu₁ arrangement. From the phenomena mentioned above, the superexchange interaction through the Cu₁-O₄-O₅-Cu₁ arrangement becomes stronger as illustrated in Fig. 6 and therefore the antiferromagnetic ordering sets in at a higher temperature than that of pure $\text{Sc}_2\text{Cu}_2\text{O}_5$ as indicated in Fig. 4.

The plots of $\chi_m T$ vs. T for $\text{Sc}_2\text{Cu}_2\text{O}_5$ and $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$ are shown in Fig. 7. In the case of $\text{Sc}_2\text{Cu}_2\text{O}_5$, $\chi_m T$ increased with decreasing temperature. This behavior indicates that the $\text{Sc}_2\text{Cu}_2\text{O}_5$ compound possesses ferromagnetic exchange coupling between Cu²⁺.⁶⁾ $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$, in contrast, showed no such maximum peak. The $\chi_m T$ decreased with decreasing temperature. The difference in the behavior of $\chi_m T$ vs. T between $\text{Sc}_2\text{Cu}_2\text{O}_5$ and $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$ explicitly reveals that the ferromagnetic interaction in $\text{Sc}_2\text{Cu}_2\text{O}_5$ is destroyed by the Co doping in $\text{Sc}_2\text{Cu}_2\text{O}_5$. The broad maximum peak at 50 K for $\text{Sc}_2\text{Cu}_2\text{O}_5$ is close to the onset temperature of antiferromagnetic interaction.

We can also calculate the Curie constant (C) from

Fig. 7. The $\chi_m T$ - T relationships for $\text{Sc}_2\text{Cu}_2\text{O}_5$ (○) and $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$ (●).

the slope of the $1/\chi_m-T$ line in Fig. 3 as well as obtain the effective magnetic moment from the Curie constant. The slopes for $\text{Sc}_2\text{Cu}_2\text{O}_5$ and $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$ are 2.39 ($C=0.418$) and 1.24 ($C=0.805$), respectively. The effective magnetic moments are calculated as 1.83 and 2.54 B.M., respectively. The effective magnetic moment and C are tabulated in Table 3 for samples with $x=0.2$ and 0.6. Both μ_{eff} and C monotonically increase with the amount of Co substitution. Since the μ_{eff} value for $\text{Sc}_2\text{Cu}_{1.6}\text{Co}_{0.4}\text{O}_5$, where one fifth of the Cu sites are replaced by Co, is 2.54 B.M., and the Co ions in the solid solution are determined to be in the divalent state from the oxygen content analysis, it is easy to deduce that the doped Co^{2+} ions are in a high spin state.

Moreover, the paramagnetic Curie temperature (θ_p) obtained from Fig. 3 deviates toward negative values with the Co^{2+} doping. Since Co^{2+} is in a high spin state, both $d_{x^2-y^2}$ and d_{z^2} are half-filled. Therefore, the doping of a high-spin Co^{2+} ion into a Cu^{2+} site hardly influences the superexchange interaction of half-filled $d_{x^2-y^2}$ in Cu^{2+} and p orbitals in O^{2-} between the Cu^{2+} ions along the a -axis. The Co doping is unrelated to the one-dimensional spin-spin interaction characteristics. In contrast, the weaker ferromagnetic interaction along the b -axis is between the half-filled $d_{x^2-y^2}$ and completely filled d_{z^2} orbitals in Cu^{2+} of adjacent chains. In the case that Cu^{2+} ions are partially substituted for Co^{2+} ions, the interaction between Cu^{2+} and Co^{2+} is between the half-filled $d_{x^2-y^2}$ orbital of Cu^{2+} and the half-filled d_{z^2} orbital of Co^{2+} . The doping of Co^{2+} into the Cu^{2+} site reduces the ferromagnetic interaction along the b -axis. This is the reason for the deviation of θ_p toward the negative direction.

In conclusion, Co^{2+} ions can substitute for both Cu_1 and Cu_2 sites of $\text{Sc}_2\text{Cu}_2\text{O}_5$ equally and can form a solid solution with x up to 0.4 in $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$. This substitution causes the enhancement of the overlap between two oxygen orbitals in the Cu-O-O-Cu arrangement along the c -axis to strengthen the antiferromagnetic coupling and leads to the increase of the Néel temperature. The weaker ferromagnetic

properties along the b -axis are partially destroyed by the doping and this results in a negative shift of the paramagnetic Curie temperature. In contrast, the doping does not affect the stronger ferromagnetic superexchange which gives rise to the one-dimensional magnetic behavior along the a -axis.

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Table 3. μ_{eff} and Curie Constant (C) for $\text{Sc}_2\text{Cu}_{2-x}\text{Co}_x\text{O}_5$

X	μ_{eff} /B.M.	C
0	1.83	0.418
0.2	2.41	0.724
0.4	2.54	0.805
0.6	3.21	1.29