Fabrication and magnetic properties of $4SC(NH_2)_2$–$Ni_{0.97}Cu_{0.03}Cl_2$ single crystals*

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Single crystals of $4SC(NH_2)_2$–$Ni_{1-x}Cu_xCl_2$ ($x = 0.03$) (Cu-DTN) containing spin $S = 1/2$ Cu^{2+} and $S = 1$ Ni^{2+} cations are synthesized by slow evaporation methods. Structural characterization demonstrates that the Cu-DTN is of a tetrahedral structure with lattice parameter c being 9.0995 Å, which is 1.32% expansion compared with that of parent material DTN due to the larger radius of the Cu ion. Direct current (DC) susceptibility measurements show that both the antiferromagnetic exchange interaction at low temperature and the large anisotropy of susceptibilities are suppressed after doping the Cu ion, which could be related to the structural distortion and the increase of the super-exchange paths in Cu-DTN.

Keywords: magnetic metal-doped, magnetic materials, susceptibility, antiferromagnetic interaction

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1. Introduction

Low-dimensional frustrated spin systems have attracted extensive attention due to their rich magnetic ground states arising from a complex interplay of thermal and quantum fluctuations. Previous studies have demonstrated that in a one-dimensional (1D) antiferromagnetic (AFM) chain system with spin $S = 1/2$, a gapless ground state would be formed.[1] However, for a 1D AFM chain system with spin $S = 1$, a finite energy gap between the lowest lying singlet ground state and the first excited triplet state might emerge.[2] So far, a lot of research on the low-dimensional AFM chain systems focused on the magnetic ions with mixed-spin states,[2–9] such as quasi-1D mixed-spin antiferromagnetic materials R_2BaNiO_5 (R = Pr, Nd or Nd_xY_{1-x}) with the $S = 1$ Ni^{2+} and the R^{3+} magnetic ions, in which the coexistence of long-range order and Haldane gap excitations was observed,[10,11] and spin-peierls system $Cu_{1-x}Cd_xGeO_3$ with a finite gap appears at the spin-peierls phase transition.[12–16]

$4SC(NH_2)_2$–$NiCl_2$ (DTN) with antiferromagnetic $S = 1$ chains of Ni^{2+} ions, is the best-known candidate for the Bose–Einstein condensation studies in magnetic fields.[17] By doping low concentration of nonmagnetic halogen Br ions in the model compound DTN, a Bose glass of field-induced magnetic quasiparticles was observed due to the induced disorder by the doped Br atoms.[18] On the other hand, in a pure spin $S = 1/2$ chain system of Cu^{2+} ions, spontaneous three-dimensional long range antiferromagnetic order will emerge, such as $(CH_3)_2NH_2CuCl_3$ (MCCL).[19,20] If the $S = 1$ Ni^{2+} ions in DTN can be replaced by other atoms with spin of half integer, such as Cu^{2+} ions, novel physical properties can be highly expected.

In this paper, we report the synthesis of the spin $S = 1/2$ Cu^{2+}-doped DTN single crystals $4SC(NH_2)_2$–$Ni_{1-x}Cu_xCl_2$ ($x = 0.03$) (Cu-DTN). The Cu-DTN with single crystalline quality exhibits a tetrahedral structure with c being 9.0995 Å, which is slightly larger than that of the parent material DTN due to the larger radius of Cu^{2+}. Magnetic measurements show that after Cu ions are doped, the broad maximum magnetic susceptibility peak shifts to low temperature, indicating the weakening of the AFM short-range order interaction, and almost isotropic magnetic properties are observed. The significant change of the magnetic behavior of the Cu-DTN is related to the structural distortion and the emergence of novel super-change paths caused by Cu^{2+} ion doping.

2. Experiment

The single crystal Cu-DTN was synthesized by the slow evaporation method in a water bath environment at a constant temperature.[21] The grown crystals were identified by x-ray powder diffraction (XRD) using Cu Kα radiation with a scanning rate of 0.02°/min. The chemical compositions were determined by energy dispersive x-ray spectrometry (EDX). The

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DC magnetic susceptibility values were measured by using a SQUID-VSM magnetometer (Quantum Design) with the magnetic field up to 7 T applied perpendicularly and parallelly to the c axis of the sample, respectively.

3. Results and discussion

3.1. Structural analysis

Figure 1(a) shows the x-ray diffraction patterns of the prepared Cu-DTN. All the diffraction patterns can be indexed to the $4SC(NH_2)_2$–$Ni_{1-x}Cu_xCl_2$ with $x = 0.03$. No other diffraction peaks were observed, indicating the high purity of the synthesized Cu-DTN. For comparison, the diffraction patterns of DTN are also collected as shown in Fig. 1(b). It can be seen that after the Cu^{2+} ions are doped, the tetragonal structure with space group $I\bar{4}$ is still maintained. The lattice parameters derived from the single-crystal XRD diffraction pattern are $a = 9.6018$ Å, $b = 9.6018$ Å, and $c = 9.0995$ Å. Comparing with the parameters of pure DTN,[22,23] after Cu^{2+} ions are doped, the c lattice parameter and a (b) axis are enlarged about 1.62% and 0.45%, respectively. The large expansion of the c lattice parameter is related to the radius of Cu^{2+} ion larger than that of Ni^{2+} ion in DTN, which can lead to structural distortion. Meanwhile, Cu^{2+} ions-doped DTN could also induce new types of super-exchange paths, i.e., Cu–Cl–Cl–Ni, Ni–Cl–Cl–Cu, and Cu–Cl–Cl–Cu, which is a prerequisite for novel magnetic properties for Cu-DTN.

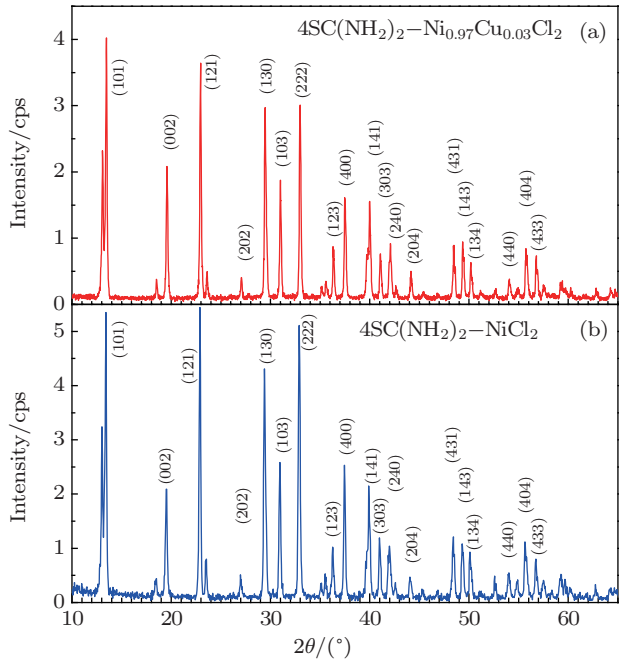


Fig. 1. (color online) The x-ray powder diffraction patterns of $4[SC(NH_2)_2]$–$Ni_{0.97}Cu_{0.03}Cl_2$ crystals (a) and $4[SC(NH_2)_2]$–$NiCl_2$ crystals (b) at room temperature.

3.2. Magnetic properties

Figure 2 shows the magnetic susceptibilities of the Cu-DTN single crystals in a temperature range from 2 K to 300 K with magnetic fields H perpendicular (χ_a) and parallel (χ_c) to the c axis, respectively. As seen in Fig. 2(a), when the magnetic field is applied along the c axis, the magnetic susceptibilities almost increase monotonically as temperature decreases. The inset shows that a broad maximum peak can be observed in a low magnetic field regime, similar to that of the magnetic susceptibility of pure DTN, which is associated with the occurrence of a short-range AFM ordering. The maximum peak that appears is determined to be $T_{max} \sim 3$ K under $H = 1$ T, which is a little smaller than that of the pure DTN (~ 6 K).[22] With magnetic field increasing, the peak shifts to a lower temperature, and no peak can be observed in the whole temperature regime when the applied magnetic field increases to higher than 5 T. The disappearance of the peak indicates that the AFM short-range order interaction is strongly suppressed under a high applied magnetic field. However, the magnetic susceptibility shows a magnetic field-independent behavior at a high temperature, and the curves almost overlapped with magnetic field changing from 0 to 7 T.

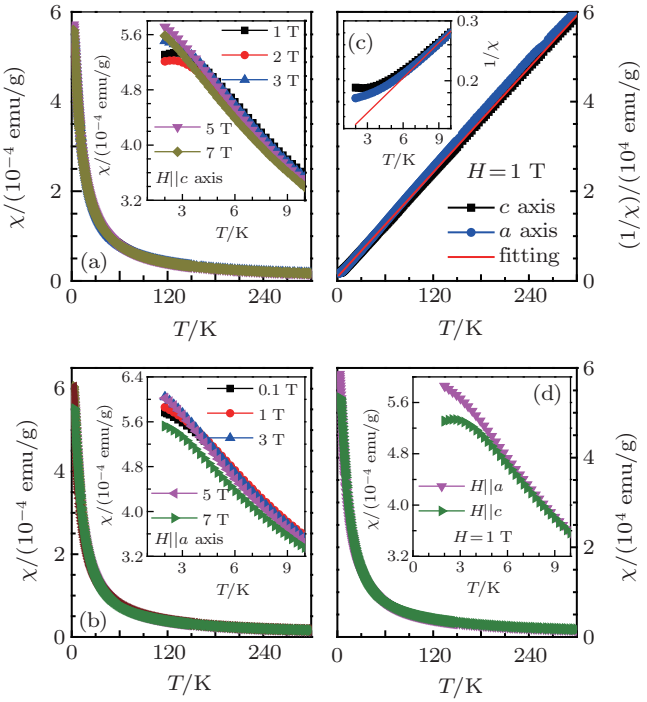


Fig. 2. (color online) Temperature-dependent magnetic susceptibilities for (a) $H \parallel c$ and (b) $H \parallel a$. (c) Curie–Weiss law (red line) fitting the reciprocal susceptibility $1/\chi_c$ (black line), the inset shows the low temperature regime (blue line denotes $1/\chi_a$). (d) Magnetic susceptibility as a function of temperature under $H = 1$ T, with magnetic field applied along c axis and a axis, respectively. Inset shows the scenarios of the low temperature regime.

The magnetic properties of Cu-DTN, with the magnetic field applied along the a axis, are also investigated as shown in Fig. 2(b). The magnetic susceptibilities also increase monotonically as temperature decreases, which is similar to that when a magnetic field is applied parallelly to the c axis. It is noted that no obvious broad maximum peak can be observed even when the temperature decreases to 2 K. However,

clear deviations between the reciprocal susceptibility and the fitted Curie–Weiss curve are shown in the inset of Fig. 2(c) for magnetic fields applied along the a axis and c axis, respectively, indicating the occurrence of the AFM correlation at low temperature. Curie–Weiss temperature is estimated to be -4.8 K from the $1/\chi$–T curves, and the negative Curie temperature further suggests the intrachain interactions in Cu-DTN are AFM correlation.

Contrary to the case of pure DTN,[2,22] the susceptibilities χ_a and χ_c of Cu-DTN are almost overlapped in the high temperature regime, indicating nearly isotropic magnetic properties of Cu-DTN as shown in Fig. 2(d). The strong suppression of the anisotropy in Cu-DTN is due to the replacement of the anisotropic Ni ions by isotropic Cu ions. The slight deviation between χ_c and χ_a at low temperature is related only to spin susceptibility whose anisotropy comes from the different magnetic interactions.

The magnetic field-dependent magnetizations of the Cu-DTN measured at 2 K are shown in Fig. 3. The magnetization exhibits similar behaviors to those when the magnetic field is applied parallelly to the c axis and a axis, respectively. An approximate linear increase with increasing magnetic field can be observed when the magnetic field is lower than 2 T, indicating the AFM exchange interaction in the Cu-DTN. When the magnetic field further increases, a characteristic change in the slope of the curve of magnetization versus magnetic field further demonstrates the suppression of the AFM exchange interaction at high magnetic field, which is consistent with the χ–T measurement in Figs. 2(a) and 2(b).

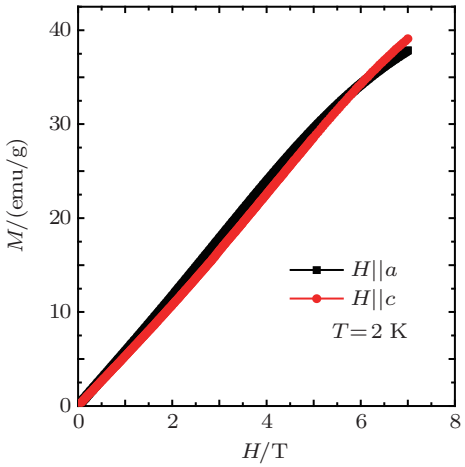


Fig. 3. (color online) Magnetic field dependences of the magnetization at 2 K for magnetic field parallel to different axes.

4. Discussion

Compared with the case of pure DTN, several intriguing magnetic properties emerge after partially replacing a Ni ion with a Cu ion, i.e. the suppression of the antiferromagnetic correlation at low temperature and the suppression of the anisotropy of the DTN.

In the pure DTN, the magnetic coupling occurs mainly through the Ni–Cl–Cl–Ni super-exchange path along the magnetic chain (c axis).[8,9] However, after doping Cu ions, the larger radius of the Cu ion than that of the Ni ion can result in the distortion of the lattice and weakening of the magnetic interaction coupling J_c. Three new super-exchange paths, i.e., Cu–Cl–Cl–Cu, Cu–Cl–Cl–Ni, and Ni–Cl–Cl–Cu with a weak bonding energy form. According to Goodenough–Kanamori rule, the exchange interaction between the magnetic ions is sensitive to the distances of R–Cl (R = Cu, Ni) and Cl$\cdots$Cl.[24–30] Therefore, by replacing the Ni ions with Cu ions of large radius, the intra-chain magnetic super-exchange interaction J_c along the c axis can decrease significantly, which results in the suppression of the AFM exchange interaction in Cu-DTN at low temperature as seen in the shift of the broad maximum magnetic susceptibilities peak to a low temperature in Fig. 2(a).

The disappearance of the large anisotropic susceptibility in Cu-DTN can be understood by taking the isotropic properties of the Cu^{2+} ions into account. The tetragonal symmetry of the DTN crystal is the premise of magnetic phase transitions BEC, in which Ni spins with the large single ion anisotropy D are strongly coupled along the tetragonal axis (c axis). The single-ion anisotropy D generates an on-site repulsion, and the magnetic field acts as a chemical potential. However, after Ni^{2+} spins are partially substituted by those of Cu^{2+} in Cu-DTN, the single-ion uniaxial anisotropy is suppressed, and the axial symmetry is also broken in the distorted structure caused by the Cu^{2+} doping.[31–33]

Considering the difference in spin state between Cu^{2+} and Ni^{2+}, the ground state of Cu-DTN also changes. After doping Cu^{2+}, four probable super-change paths, i.e., Ni–Cl–Cl–Ni, Cu–Cl–Cl–Cu, Cu–Cl–Cl–Ni, and Ni–Cl–Cl–Cu, will be formed, disordered, and distributed due to the random replacement of Ni^{2+} by Cu^{2+}. It is noted that the two new kinds of super-change paths, i.e., Cu–Cl–Cl–Ni and Ni–Cl–Cl–Cu, are composed of magnetic ions with $S = 1/2$ (Cu^{2+}) and $S = 1$ (Ni^{2+}), respectively, and the interaction along these two paths is different from that between Cu–Cl–Cl–Cu with gapless ground state and Ni–Cl–Cl–Ni with finite gap ground state. For instance, due to the correlations between inter- and intra-chains interactions and the frustration effects of spins and lattice significantly changed after doping Cu^{2+} ions, the long-range AFM order is expected. However, due to the limitation of the experiment setup, the magnetic properties neither in ultralow temperature regime nor in higher field can be detected now, which are still worth further exploring.

5. Conclusions

The crystal structure and magnetic properties of Cu doping DTN are studied. Compared with the pure DTN, Cu-

DTN has the same crystal structure while the lattice parameters slightly expand due to the larger radius of Cu^{2+} ions. The reciprocal susceptibilities $1/\chi_c$ and $/\chi_a$ exhibit a Curie–Weiss behavior at high temperature with a Curie–Weiss temperature of -4.8 K and the AFM short-range order correlation at low temperature. The susceptibility with the downward shift of the maximum peak shows the weak anisotropy, indicating the weaker intra-chain magnetic interactions induced by doping Cu^{2+} and the suppressed large single-ion anisotropy of Ni^{2+} ions.

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