Magnetic properties and magnetocaloric effect of the Cr-based spinel sulfides $Co_{1-x}Cu_xCr_2S_4$*

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Crystallographic structure, magnetic properties, and magnetic entropy change of the Cr-based spinel sulfides $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$–0.8) have been investigated. All these compounds crystallize into the cubic spinel structure, the Cu substitution shrinks linearly the lattice constant at a ratio of 0.0223 Å per Cu atom in the unit cell, and enhances linearly the Curie temperature and the spontaneous magnetization at the rates of 18 K and 0.33 μ_B/f.u. per Cu atom in the unit cell, respectively. All these compounds show a typical behavior of second order magnetic transition, and a room temperature magnetic entropy change of 2.57 J/kg·K is achieved for $Co_{0.4}Cu_{0.6}Cr_2S_4$.

Keywords: chalcospinels, magnetocaloric effect, magnetism, crystal structure

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1. Introduction

Materials with giant magnetocaloric effect (MCE) close to room temperature (RT) are expected to be applied in magnetic refrigerators, air conditions, and medical fields, due to their high energy efficient and environmentally friendly benefits.[1–3] A lot of magnetic materials hold giant MCE with first-order magnetic transition have been discovered.[4,5] However, the irreversibility of these first-order magnetic entropy change materials limits their practical application. Thus, materials with large second-order magnetic entropy change are demanded since they generally exhibit a great reversible behavior in the magnetization as a function of temperature and magnetic field. Recently, ferromagnetic spinel sulfides ACr_2S_4 (A = Zn, Cd, Mn, Fe, Co, Ni, Cu, etc.) have attracted much attention due to the discovery of colossal magnetocapacity, large magnetoresisitance, relaxation multiferrorics, large magnetooptical Kerr effect, and large magnetic entropy change.[6–15] We have reported a large reversible secondary magnetic entropy change of $-\Delta S_m = 7.04$ J/kg·K in $CdCr_2S_4$ at the temperature of near Curie temperature (T_C) with an applied field variation from 0 to 5 T, which makes it a potential magnetic refrigeration material.[13] However, the $CdCr_2S_4$ magnetic phase transition occurs around the low T_C of 87 K,[13] far below the RT.

The previous works have proved that $CuCr_2S_4$ is a ferromagnetic metal with T_C of 377 K,[16,17] and $CoCr_2S_4$ is a ferrimagnetic n-type semiconductor with a critical temperature of 227 K.[18] Thus, one can speculate that a solid solution with T_C near RT can be obtained by substituting Cu for Co in $CoCr_2S_4$. In the present work, a series of solid solutions $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$–0.8) were synthesized by the traditional solid state reaction, and the impact of Cu substitution in the $CoCr_2S_4$ compound in terms of magnetic phase transitions and MCE was studied.

2. Experiment

$Co_{1-x}Cu_xCr_2S_4$ ($x = 0$, 0.2, 0.4, 0.6, 0.8) compounds were synthesized by solid state reaction at elevated temperatures. Mixtures of CoS (99.9%, Alfa), CuS (99.9%, Alfa), and Cr_2S_3 (99.98%, Alfa) powders with appropriate stoichiometry were ground in an agate mortar, then the grinded mixture was pressed into pellets, and sealed into a quartz tube filled with highly purified argon gas. Finally, the pellets were sintered at 775 K for two days, followed by 1025 K for three days with a heating rate of 5 K/min. The samples were cooled down to RT by natural cooling prior to removal from the furnace.

The powder x-ray diffraction (XRD) patterns of $Co_{1-x}Cu_xCr_2S_4$ were recorded with 2θ from 10° to 70° at RT on a Bruker D8 x-ray diffractometer equipped with a Cu-$K\alpha$ radiation source operated at 40 kV and 40 mA, and the intervals were 0.015° per step. These XRD data were analyzed using Rietveld refinement[19] method by GSAS-EXPGUI software package.[20] The magnetization measurements were performed by a quantum design magnetometer superconduct-

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ing quantum interference device (SQUID). The magnetization data were collected from 4 K to 400 K under an applied magnetic field of 500 Oe, and the magnetization versus magnetic field (M–H) data of $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$, 0.6, 0.8) were collected at temperature near T_C, with applied magnetic field variation from 0 T to 5 T. For the M–H measurements, the temperature step was 5 K over the whole regions and the sweep rate of the magnetic field was 10 Oe/s.

3. Results and discussion

The structure and phase purity of $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$, 0.2, 0.4, 0.6, 0.8) have been examined by XRD measurements. Note that the single-phase compound $CuCr_2S_4$ was not obtained with the same synthesis procedure due to the easy formation of the impurity phase $CuCrS_2$ which has similar phase crystallization temperature with $CuCr_2S_4$.[21] Figure 1 shows the refined XRD pattern of the parent $CoCr_2S_4$. The structural parameters of the fcc-cubic spinel structure with space group Fd-3m (No.227) were used as the inputs in the refinement. The pattern determined is statistically in agreement with the observed data, and the refinement profile agreement factors are $R_p = 9.98\%$, $R_{wp} = 13.19\%$, and $\chi^2 = 1.285$. All $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$, 0.2, 0.4, 0.6, 0.8) XRD patterns are plotted in Fig. 1. At the first glimpse, the major diffraction peaks, indexed as (220), (311), (400), (511), and (440) for $CoCr_2S_4$, are duplicated for other x concentration samples. The same refinement process was then done on all other samples, and the similar agreement factors were also obtained, which indicates a pure spinel phase. The reasonable refinement results verify that all these compounds crystallize into pure cubic spinel structure at RT. The refined lattice parameters a, b, c and the calculated unit-cell volume are listed in Table 1, and plotted in Fig. 2. It can be found that the lattice constants a, b, c and the unit cell volume V decrease linearly with an increase of x in accordance with the Vegard's law,[22,23] indicating that our samples are good solid solutions. This result is reasonable since the tetrahedral site Co^{2+} ($r = 0.58$ Å) has a little larger radius than that of the tetrahedral site Cu^{2+} ($r = 0.57$ Å).[24] We demonstrated that the Cu substitution linearly shrinks the lattice constant at a ratio of 0.0223 Å and the unit cell volume at a ratio of 6.4 Å^3 per Cu atom substituted in the unit cell by fitting these refined parameters.

Table 1. The lattice parameters, the Curie temperature, the spontaneous magnetization, and the magnetic entropy change of the spinel compounds $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$–0.8).

x	a/Å	V/Å^3	T_C/K	M_s/μ_B·f.u.$^{-1}$	$-\Delta S_m$/J·kg^{-1}·K^{-1}
0.0	9.917(6)	975.3(1)	225	1.9	3.33
0.2	9.884(1)	965.6(3)	250	2.4	–
0.4	9.841(4)	953.2(1)	271	3.0	–
0.6	9.820(7)	947.2(2)	303	3.4	2.57
0.8	9.777(3)	934.6(4)	339	4.1	2.05

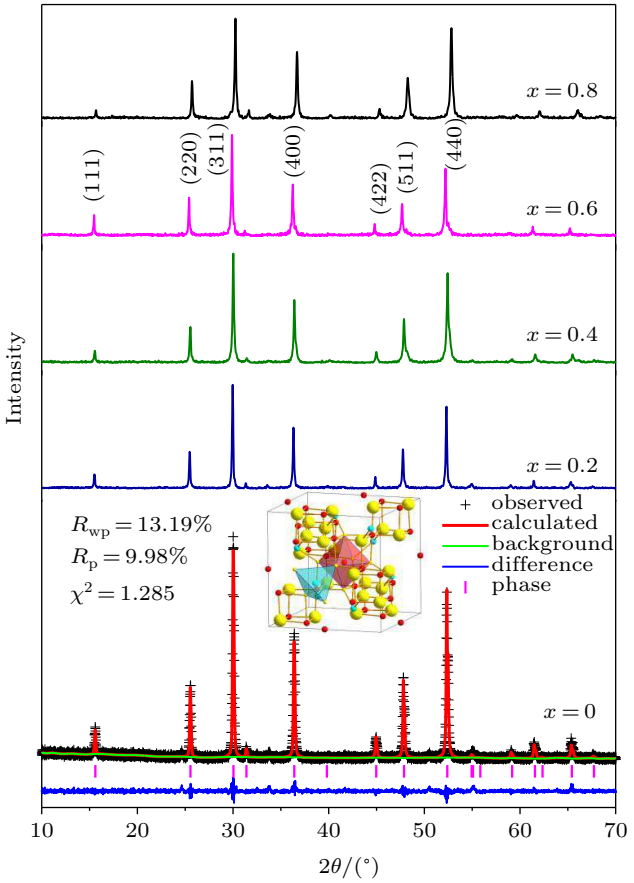


Fig. 1. (color online) Powder x-ray diffraction (XRD) patterns of $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$, 0.2, 0.4, 0.6, 0.8) measured with a Cu-$K\alpha$ source on a Bruker D8 instrument at RT. Bottom panel is the Rietveld refinement XRD pattern of the parent $CoCr_2S_4$ sample. Observed intensity and calculated intensity are represented by black cross signs and red solid line. The magenta bar represents the Bragg peaks position and the blue curve at the bottom represents the residual (observed intensity minus calculated intensity difference). The green line is the background used in the refinement. The inset shows the spinel-type crystal structure of ACr_2S_4 (A: cyan, Cr: red, S: yellow).

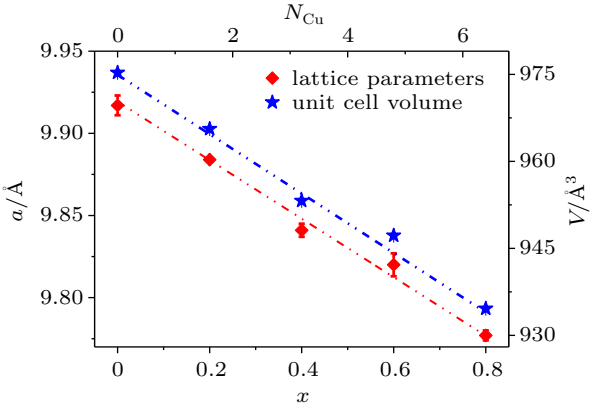


Fig. 2. (color online) The refined lattice parameters and unit cell volume of $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$, 0.2, 0.4, 0.6, 0.8) as a function of Cu concentration x and the number of Cu atoms per unit cell N_{Cu}. Some data error bars are too small to be visible. The Cu substitution shrinks linearly the lattice constant at a ratio of 0.0223 Å per Cu atom substituted in the unit cell and the unit cell volume at a ratio of 6.4 Å^3 per Cu atom substituted in the unit cell.

Figure 3(a) shows the temperature-dependent magnetization of $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$–0.8) from 4 K to 400 K under an external magnetic field of $H = 500$ Oe. From the

curve shape, all samples are seemingly ordered in a typically ferro- or ferrimagnetic configuration below their phase transition temperatures. The Curie temperatures T_C defined as the maximum slope in the M–T curves, obtained by analyzing the first order derivative of the curve, are listed in Table 1 and plotted in Fig. 3(b) as a function of the Cu concentration x and the number of Cu atoms per unit cell N_{Cu}. T_C (= 225 K) for $CoCr_2S_4$ is in a good agreement with the previous work,[18] and increases to 339 K for $x = 0.8$ linearly with a slope of 18 K per Cu atom substituted in the unit cell. It is worth to note that T_C of 303 K for $x = 0.6$, quite near to RT, implies that it might be a potential candidate used as a RT magnetic refrigeration material.

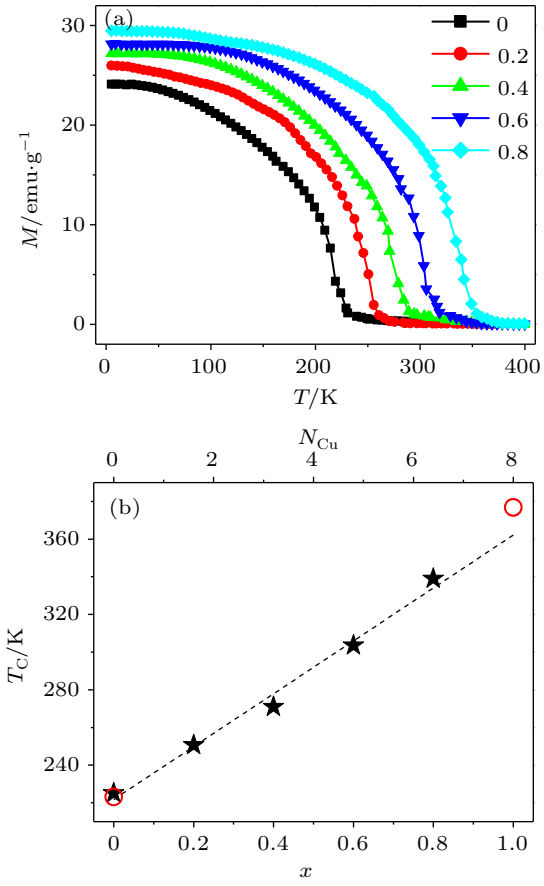


Fig. 3. (color online) (a) Temperature dependence of magnetization of $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$, 0.2, 0.4, 0.6, 0.8) from 4 K to 400 K under an applied magnetic field of 500 Oe. (b) The linear relationship between the reduced magnetic phase transition temperature T_C and the Cu concentration x and the number of Cu atoms per unit cell N_{Cu}. The red open dots are experiment measured values by other researchers.[16–18]

The magnetization of $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$–0.8) as a function of the external magnetic field was taken at 5 K to determine the spontaneous magnetization. As seen in Fig. 4(a), the magnetization curves look like typical ferromagnetic, and the spontaneous magnetizations derived from the extrapolation of the magnetization at high fields to $H = 0$ are summarized in Table 1. As shown in Fig. 4(b), the spontaneous magnetization also increases linearly from 1.9 μ_B/f.u. for $x = 0$ to 4.1 μ_B/f.u. for $x = 0.8$, which is approximately in agreement with the previous works.[15,25] Therefore, one can infer that the moments of the Co and Cr atoms are antiparallel alignment with the values of 2.750 μ_B and 2.325 μ_B, respectively, with the hypothesis of non-magnetic Cu atom.

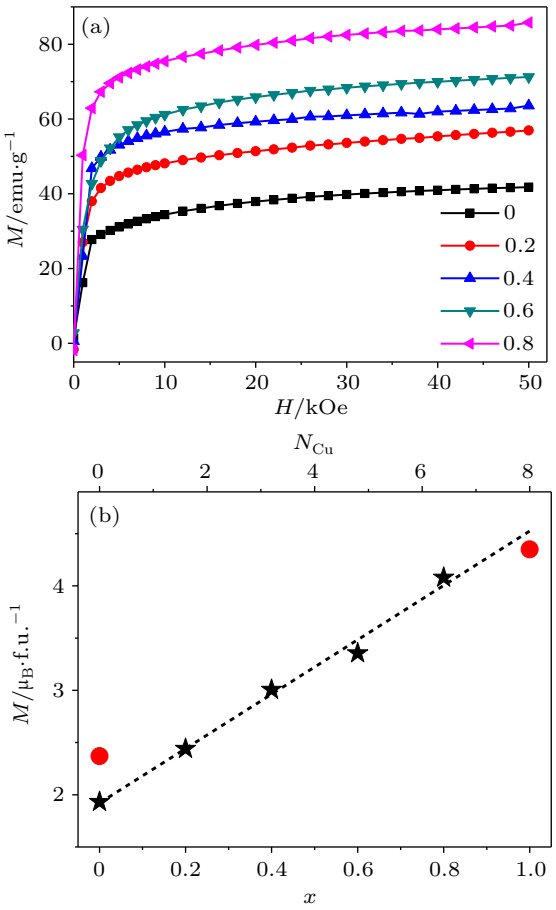


Fig. 4. (color online) (a) Magnetization versus magnetic field (M–H) of $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$–0.8) measured on the applied magnetic field from 0 T to 5.0 T at 4 K. (b) The corresponding spontaneous magnetization derived from the extrapolation of the magnetization from high fields to $H = 0$ as a function of Cu concentration x and the number of Cu atoms per unit cell N_{Cu}. The red circle dots are experiment measured values by other researchers.[15,25]

The isothermal magnetization curves of the selected $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$, 0.6, 0.8) were recorded at temperatures near their T_C's with applied magnetic field up to 5.0 T (as shown in Figs. 5(a)–5(c)). Arrott plot (i.e., M^2–H/M) is usually used for characterizing the order of magnetic phase transition.[26,27] Generally, for a first-order magnetic phase transition, the negative slope or inflection point will be found in the Arrott plot, otherwise the transition will be a second-order type. The Arrott plots of the compounds $Co_{1-x}Cu_xCr_2S_4$ are displayed in Figs. 5(d)–5(f), where neither the inflection point nor the negative slope appears above T_C. It suggests that all the magnetic phase transitions are the second-order.

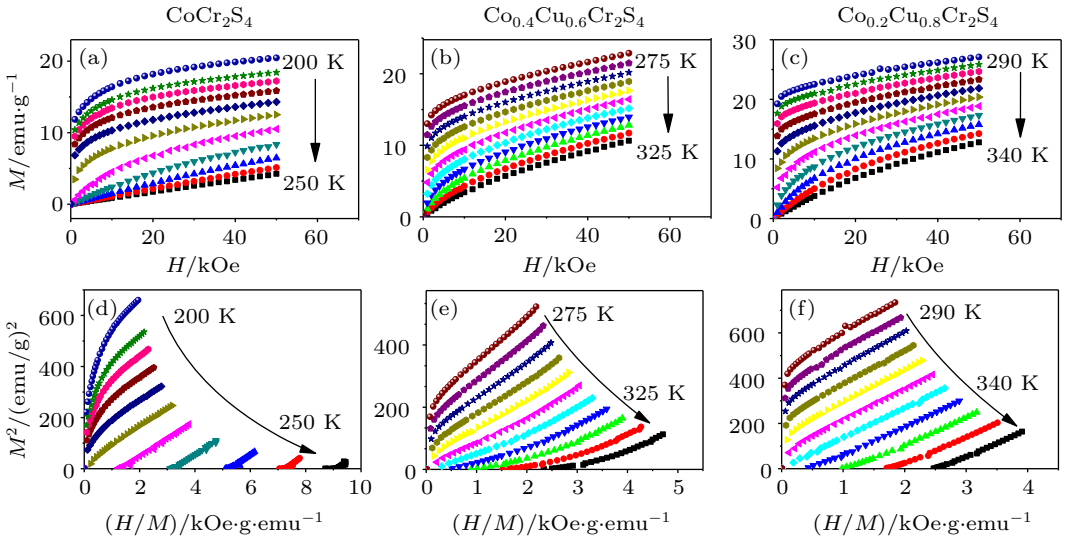


Fig. 5. (color online) (a)–(c) Magnetization versus magnetic field (M–H) measurements and (d)–(f) the corresponding Arrott plots of $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$, 0.6, 0.8) at temperature close to their Curie temperatures, respectively.

Based on the thermodynamical theory,[28] the magnetic entropy change is given by

$$\Delta S_{\rm m}(T,H) = S_{\rm m}(T,H) - S_{\rm m}(T,0) = \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H {\rm d}H. \quad (1)$$

In the case of the magnetization measurements made at constant temperature T for successive values of magnetic field H, the above equation can be approximated by the following expression:

$$\Delta S_{\rm m} = \sum_i \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i, \quad (2)$$

where M_{i+1} and M_i are the magnetization values measured in an external filed H at temperatures T_{i+1} and T_i, respectively. The accuracy of $\Delta S_{\rm m}$ calculated using this method is about 3%–10%.[29] By using the above equation, the entropy change $\Delta S_{\rm m}$ as a function of temperature of $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$, 0.6, 0.8) has been calculated upon an applied magnetic field change of 5.0 T (as shown in Fig. 6). The maximum $-\Delta S_{\rm m}$ values, close to their corresponding $T_{\rm C}$, are 3.34 J/kg·K, 2.57 J/kg·K, and 2.04 J/kg·K for $x = 0$, 0.6, and 0.8, respectively. The $-\Delta S_{\rm m}$ exhibits a λ-shaped peak around the Curie temperature, in accord with the nature of a second order phase transition.

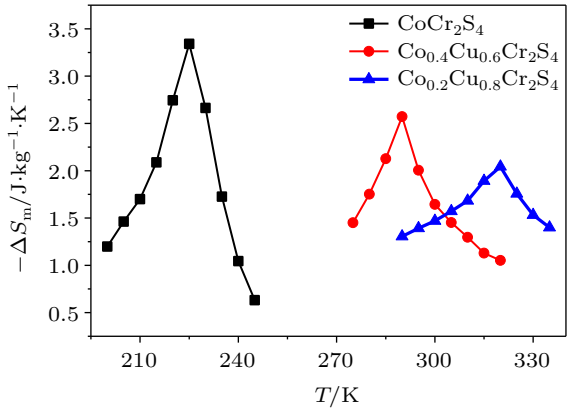


Fig. 6. (color online) Magnetic entropy change of $Co_{1-x}Cu_xCr_2S_4$ ($x = 0$, 0.6, 0.8) as a function of temperature upon an external field change of 5 T.

4. Conclusion

Single phase $Co_{1-x}Cu_xCr_2S_4$ spinel compounds with $x =$ 0–0.8 have been prepared by the traditional solid reaction method. The copper substitution results in the linear decrease of the unit cell volume with a slope of 6.4 Å^3, while the linear increase of the Curie temperature and the spontaneous magnetization with a rate of 18 K and 0.33 $\mu_{\rm B}$/f.u. with one Cu atom substitution in the unit cell, respectively. It seemingly implies a close interplay between magnetic interaction and crystallographic structure. These compounds show a typical behavior of second order magnetic transition, and the RT magnetic entropy change of 2.57 J/kg·K is achieved for the solid solution $Co_{0.4}Cu_{0.6}Cr_2S_4$, indicating the potential application as an RT active magnetic refrigerant.

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