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Magnetic transitions in delafossite $CuFeO_2$: A magnetocaloric effect study

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ABSTRACT

$CuFeO_2$ was synthetized by a solid-state reaction and its low temperature magnetic properties investigated using the magnetocaloric effect. Magnetic susceptibility measurements show that there are two magnetic transition temperatures at about 16 and 11 K. Measurement of isothermal magnetization curves for different applied magnetic fields near these temperatures show a reversal in the magnetization trend around 11 K, and Arrott plots indicate they are accompanied by second- and first-order magnetic phase transitions, respectively. Both normal and inverse magnetocaloric effects are observed, and the maximum magnetic entropy change is obtained at 11 K.

1. Introduction

The multiferroic delafossite, $CuFeO_2$, is a geometrically frustrated material with a layer structure and space group R-3m; it undergoes successive magnetic transitions with decreasing temperature, from a paramagnetic phase to a partially disordered phase (around 16 K, T_{N1}), and finally to an antiferromagnetic phase (around 11 K, T_{N2}) [1,2]. The T_{N1} and T_{N2} correspond to the point of maximum χ and an abrupt decrease in χ, respectively in the (χ-T) susceptibility curve of $CuFeO_2$, [3–5]. Although the mechanism for the magnetic behavior of $CuFeO_2$ is still under investigation, synchrotron X-ray diffraction patterns and neutron scattering observations indicate these two magnetic transitions are accompanied by second- and first-order structural phase transitions respectively [6,7]. The magnetocaloric effect (MCE) can be quantified by determining the isothermal magnetic entropy change (ΔS), which can be calculated from the total entropy S at different temperatures, and changes in ΔS often accompany magnetic transitions, including first- [8,9] and second-order transitions [10, 11]. Furthermore, the MCE has proven to be a powerful tool for probing the nature of complex magnetic ground states [12–15], but until now, equivalent studies are not available for $CuFeO_2$. Thus the present work has used the MCE to investigate the low temperature magnetic properties in synthetic $CuFeO_2$ sample, and its magnetic refrigeration potential at low temperatures is also assessed.

2. Experimental

$CuFeO_2$ sample was synthetized by a solid state reaction. High-purity (99.99%, Sinopharm Chemical Reagent Co., Ltd) powders of Fe_2O_3 and CuO were mixed thoroughly at a stoichiometric ratio and preheated at 850 °C for 15 h in air. These powders were then pressed into pellets (∼15 mm diameter and 1 mm thick) and sintered at 950 °C in an argon atmosphere for 24 h. The crystal structure of a powder sample of the synthesized $CuFeO_2$ was confirmed by X-ray diffraction (XRD) using Cu-Kα radiation at room temperature. Magnetic susceptibility measurements were performed as a function of temperature in the range of 4–300 K using a physical property measurement system with a vibrating sample magnetometer (PPMS, Quantum Design) under an applied magnetic field of 0.5 T after zero field cooling (ZFC) and field cooling (FC) to 4 K. The relationship between isothermal magnetization and magnetic field was also determined at 6 T, the highest applied field.

3. Results and discussion

The measured and calculated powder XRD patterns for the $CuFeO_2$ sample at room temperature are shown in Fig. 1. The diffraction peaks can be indexed as a single rhombohedral delafossite phase of $CuFeO_2$ (PDF#04-007-2807, R-3m space group), and there is no evidence of any impurity or secondary phase. The lattice parameters $a = b = 3.0350$ Å and $c = 17.1695$ Å were determined by Rietveld refinement of the XRD data, and are in a good agreement with the values reported by Mugnier and Amrute et al. [16,17].

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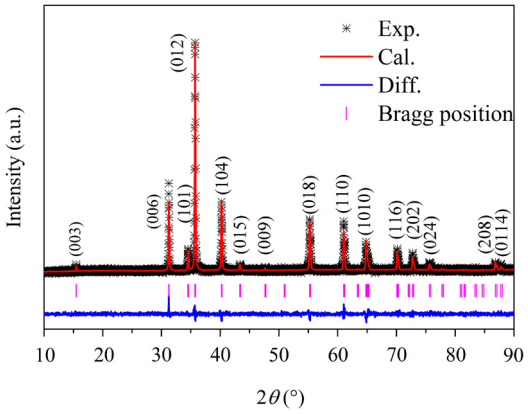

Fig. 1. Measured data (crosses) and calculated profile (continuous line overlying the crosses) of the powder XRD pattern of $CuFeO_2$. The bottom curve shows the difference between the observed and calculated intensities. $R_{WP} = 10.65\%$, $R_P = 8.46\%$.

The curves for ZFC and FC magnetic susceptibility (χ) versus temperature (T) for $CuFeO_2$ at 0.5 T are shown in Fig. 2a. The shapes of these χ-T curves are similar for both ZFC and FC with χ increasing monotonously with decreasing temperature from 300 to ~20 K, thus the high temperature paramagnetic phase obeys the Curie-Weiss law. However, on cooling from 20 to 4 K, two magnetic transition temperatures were observed at $T_{N1} = 16$ K and $T_{N2} = 11$ K (as shown in Fig. 2b), corresponding to the maximum and an abrupt drop in the χ-T curve, respectively [3–5]. This result is consistent with the previous reports [1,18]. The T_{N2} indicates the presence of an MCE, and occurs at the same temperature as the first-order structural phase transition from hexagonal to monoclinic symmetry [6]. It can also been seen from Fig. 2a that the FC-ZFC curves do not overlap, and spontaneous magnetization induced by the applied magnetic field cannot be discounted for temperatures ≤300 K. We calculated the Curie-Weiss temperatures (θ) from the χ^{-1}-T curves (Fig. 2c), and the negative θ values ($\theta = -134$ and -128 K for ZFC and FC, respectively.) show that the dominant magnetic interactions for $CuFeO_2$ at low temperatures are antiferromagnetic.

Curves for the dependence of isothermal magnetization on the applied magnetic field are shown in Fig. 3. Interestingly, the trend in the magnetization changes around the upper magnetic transition temperature. It increases with increasing temperature in the $T < T_{N1} = 16$ K region (Fig. 3a), and its rate of change reaches a maximum around $T_{N2} = 11$ K, whereas above T_{N1} the magnetization decreases with increasing temperature (Fig. 3b). These results suggest that the increasing trend in magnetization below T_{N2} is closely related to the dominant antiferromagnetic order, and that above T_{N1} there is an inverse MCE.

Arrott plots are used to characterize magnetic phase transitions, and are shown in Fig. 3c for $CuFeO_2$. For MCE materials, the Banerjee criterion [19] states that first- and the second-order magnetic transitions can be differentiated by negative or positive slopes of Arrott plots, respectively. As shown in Fig. 3c, the negative slope of M^2-H/M curves (in the $T = 3$–11 K) range indicates that $CuFeO_2$ undergoes a first order phase transition at low temperature. Conversely, the positive slope of the M^2-H/M curves at $T > T_{N1} = 16$ K corresponds to a second-order phase transition, although they are close to vertical because of the dominant paramagnetic state at high temperatures [20]. Thus these results are consistent with the high-resolution synchrotron x-ray and neutron scattering results of Ye et al. [6].

For further information the nature of magnetic ordering in $CuFeO_2$, and in order to assess its potential for magnetic refrig-

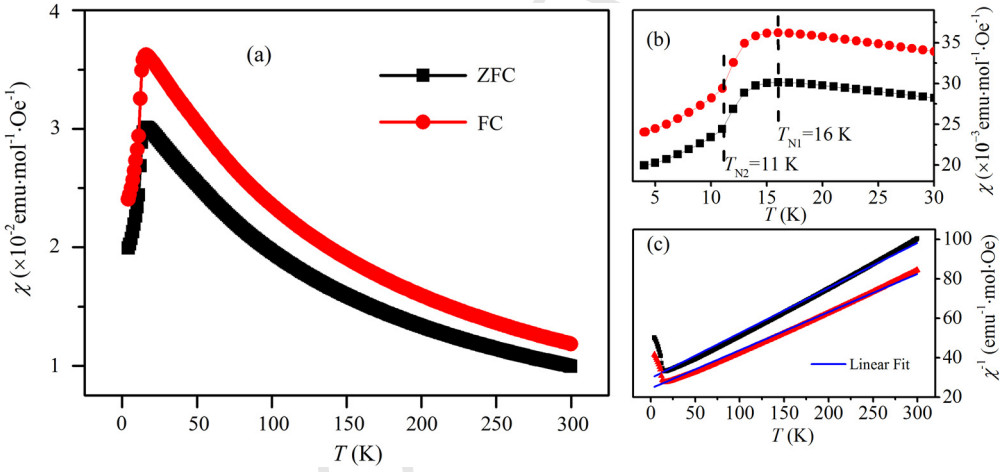

Fig. 2. ZFC and FC (a) magnetic susceptibility (χ) and (c) reciprocal magnetic susceptibility (χ^{-1}) versus temperature (T) for $CuFeO_2$ at 0.5 T, (b) is the local enlargement of the magnetic transitions.

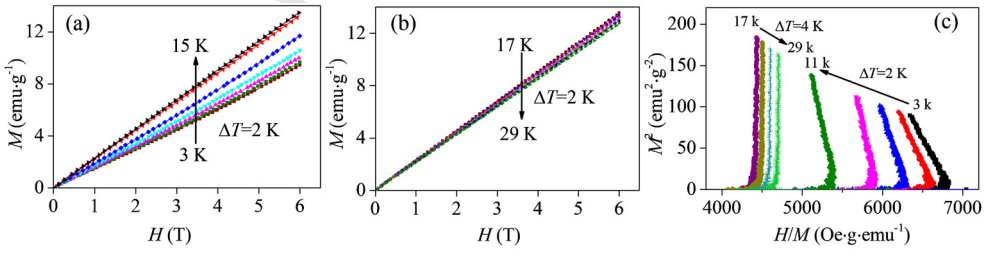

Fig. 3. Dependence of magnetization in $CuFeO_2$ on the external magnetic field for temperatures (a) ≤15 K, and (b) ≥17 K, and (c) Arrott plots of M^2 versus H/M at different temperatures.

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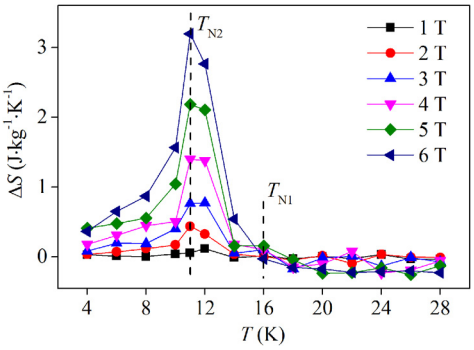

Fig. 4. Magnetic entropy changes (ΔS) versus temperature for $CuFeO_2$ under different applied fields.

eration at low temperatures, magnetic entropy changes (ΔS) were evaluated using the Maxwell's thermodynamic relationship based on magnetic isotherms in different applied fields [21]. Results for the range 1–6 T are shown in Fig. 4. There is a small negative value for ΔS above 16 K, which corresponds to the small rate of change in isothermal magnetization shown in Fig. 3b. Conversely, there are clear positive values for ΔS below 16 K, and the slope of this curve is greater on the high temperature side than at lower temperatures. It is well known that positive ΔS values are associated with antiferromagnetic ordering and result from orientational disorder in applied field [22,23]. Therefore, the positive ΔS values obtained for $CuFeO_2$ demonstrate a dominant antiferromagnetic ordering at $T < T_{N1} = 16$ K, which agrees with the calculated θ results, and also demonstrates the first transition at 16 K involves antiferromagnetic coupling, and the suitability of choosing the point of maximum χ (in χ-T curves) as T_{N1} [2–5]. A maximum ΔS value of 3.2 J·kg^{-1}·K^{-1} is achieved at 6 T with a temperature of 11 K, which corresponds to the rapid change of magnetization in the field-induced first order partially disordered to antiferromagnetic transition. This value is significantly larger than those observed at the same temperature in perovskite-type oxides, such as $EuCrO_3$ [24], $Sm_{1-x}Ca_xMnO_3$ ($x = 0.5$–0.7) [25] and $YCr_{0.85}Mn_{0.15}O_3$ [26]. However, the maximum relative cooling power (RCP) value of ~12.6 J·kg^{-1} calculated by integrating the magnetic entropy change [27] at 6 T is still too small for low temperature refrigeration applications. For geometrically frustrated materials, it has been reported that the ΔS and RCP values can be enhanced by suppression of the randomness of magnetic interaction [25,28,29]. Thus, the stable charge-ordered antiferromagnetic ground state in $CuFeO_2$ at low temperatures may be responsible for the small ΔS and RCP values.

4. Conclusions

The single-phase multiferroic compound $CuFeO_2$ synthesized by a simple solid state reaction crystallizes in the delafossite-phase structure (R-3m space group) with lattice parameters $a = b = 3.0350$ Å and $c = 17.1695$ Å. It undergoes two successive magnetic transitions at about $T_{N1} = 16$ K and $T_{N2} = 11$ K respectively. The magnetization increases with increasing temperature in the range 4 to 15 K, and its rate of change is largest around T_{N2}. Analyses of M^2-H/M curves show that there is a dominant first order magnetic phase transition at low temperature (T_{N2}); whereas the magnetic transition at T_{N1} is second order. These results represent the first observation of a MCE near magnetic transition temperatures; they show a maximum ΔS value of 3.2 J·kg^{-1}·K^{-1} at $T_{N2} = 11$ K and a RCP value of about 12.6 J·kg^{-1} in an applied magnetic field of 6 T.

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