Regulation of Cr$^{3+}$ doping on the defect characteristics and magnetic order in the CuFe$_{1-x}$Cr$_x$O$_2$ ceramics

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ABSTRACT

The defect characteristic and magnetic properties of CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0–0.4$) compounds have been investigated in detail. The results demonstrate that Cr$^{3+}$ ions enter into the CuFeO$_2$ lattice sites and induce local lattice contraction but do not change the valance state of Cu$^+$ and Fe$^{3+}$ ions. We calculate the positron annihilation lifetime in the bulk and vacancy defect trapping states by the atomic superposition method in $3 \times 3 \times 1$ CuFeO$_2$ super-cell. Combined with theoretical calculation results, the positron annihilation results indicate that the positrons are mainly annihilated in vacancy clusters in CuFe$_{1-x}$Cr$_x$O$_2$. The substitution of Cr$^{3+}$ for Fe$^{3+}$ ions decreases the open volume and increases the concentration of vacancy defects but does not change the integral defect surroundings at annihilation sites. Magnetization measurements manifest that doping with Cr$^{3+}$ reduces the antiferromagnetic transition temperature and promotes the formation of short-range magnetic correlation. Meanwhile, the enhanced short-range magnetic correlation in Cr$^{3+}$-doped CuFeO$_2$ is more readily driven by thermal activation energy and a faster dynamic behavior can be seen in time windows.

1. Introduction

In the process of seeking new functional materials, the low-dimensional delafosite ternary oxides (ABO$_2$) provide a large family of candidates due to their interestingly photoelectric, magnetoelectrical, and thermoelectric properties [1–4]. These ABO$_2$ oxides are exemplary p-type wide-bandgap semiconductors, widely applied in transparent conducting oxide field for their unique integration of electrical conductivity and optical transparency [5]. They crystallize in a layered structure, in which the trivalent cations B coordinated with the oxygen octahedron are separated by monovalent cations A in a dumbbell-shaped configuration along the c-axis [6,7]. Generally, these compounds belong to space group P6$_3$/mmc (the hexagonal 2 H orR3m (the rhombohedral 3 R) depending on the stack fashion of the oxygen layers along the c-direction [8]. This structure configuration is in favor of the magnetic properties, such as step-like magnetic phase transitions and multiferroic properties, as a result of a strong geometrical frustration occurring in the magnetic triangular lattice B sites. Among the ABO$_2$ groups, the best-known multiferroic materials are the CuFeO$_2$ and CuCrO$_2$ compounds, which have been extensively reported since they are exemplary frustrated triangular lattice antiferromagnets deriving from Fe$^{3+}$ ($S = 5/2$, $t_{2g}^3e_g^2$) and Cr$^{3+}$ ($S = 3/2$, $t_{2g}^3$), respectively. As usual multiferroic materials, these two compounds are expected to exhibit a potential application prospect, including magnetic sensor devices [9], high capacity storage devices [10,11], catalysts [12], electrodes materials [13] and thin-film devices [14]. The nature difference in these two compounds, underlies in the fashion where the magnetic ground state is formed by the distinctive magnetic ions order. In the case of CuFeO$_2$, two successive antiferromagnetic transitions are observed in zero-field according to the previous powder neutron diffraction [15]. As the temperature increases in zero-field, Fe$^{3+}$ ions order in an Ising-like four-sublattice (4SL, $I\uparrow\downarrow\uparrow\downarrow\downarrow$) configuration below $T_{N2} \sim 11$ K, then transform into the paramagnetic (PM) state above $T_{N1} \sim 15$ K through a sinusoidal amplitude-modulated quasi-long range antiferromagnetic spin structure [6,15–19]. It is universally acknowledged that a slight perturbation such as the external magnetic field or foreign ions can obviously change the magnetic structure because of the unique frustrated structure. With the application of an external magnetic field, a sequence of magnetic orders are observed below $T_{N2}$ at different critical fields of $B_{c1} \sim 70$ kOe, $B_{c2} \sim 130$ kOe, $B_{c3} \sim 200$ kOe, $B_{c4} \sim 340$ kOe and $B_{c5} \sim 490$ kOe, respectively [20–22]. Among the above interval, the field barely among $B_{c1}$–$B_{c2}$, CuFeO$_2$ exhibits ferroelectric-incommensurate (FEIC) phase with the spiral spin order that is the origin of ferroelectric polarization on account of the
magnetoelastic effect. And remarkably, this FEIC phase can be mimicked by substituting a fraction of nonmagnetic cations in the Fe sites without applied magnetic field in the recent literature [17,19,23–25]. These foreign ions (S = 0), such as Al$^{3+}$, Ga$^{3+}$ and Rh$^{3+}$, are very efficient at converting the ground state from 4SL $\uparrow \downarrow \downarrow \downarrow$ into FEIC phase. In contrast to the isostructural CuFeO$_2$, Cr$^{3+}$ ions in CuCrO$_2$ adapting a typical Heisenberg triangular lattice, order into an incommensurate proper screw configuration with the magnetic modulation vector $q$ along the [110] direction below $T_n \approx 24$ K [26]. This distinctive configuration is very similar to the one found in FEIC phase of CuFeO$_2$. But unfortunately, the relevant magnetic researches are rarely reported with regard to Cr doped CuFeO$_2$ system. Ruttanapun C [27], reported that the electronic, thermoelastic and optical properties are significantly influenced by the atomic layer structure and lattice strain occurring due to the introduction of Cr$^{3+}$ ions. In the same year, Mori K [28], proposed that the magnetic transition temperature increases and the magnetization enlarges as the Cr$^{3+}$ contents increase. However, up to now, the mechanism of Cr$^{3+}$ substitution for Fe$^{3+}$ ions on CuFeO$_2$ magnetic properties is still unclear.

The Cr$^{3+}$ ions can readily enter into CuFeO$_2$ lattice and can be randomly distributed at the Fe sites because of the relatively stable valence state and the similar radius between Fe$^{3+}$ and Cr$^{3+}$ ions, and the disordered Fe/Cr at the B site is of benefit to the three random magnetic interaction of Fe-Fe, Fe-Cr and Cr-Cr. These random interactions make the magnetic state shear intricate. Therefore, it is fascinating to explore the mechanism of Cr$^{3+}$ doping effect on CuFeO$_2$ system. In this paper, we carry out a comprehensive study of the defect characteristics and magnetic properties of the CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0$–$0.4$) series.

2. Materials and methods

Polycrystalline CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0$, 0.1, 0.2, 0.3 and 0.4) samples were synthesized using direct solid-state reaction. Briefly, stoichiometric amounts of high-purity analytical grade ($\geq 99.99\%$) CuO, Fe$_2$O$_3$ and Cr$_2$O$_3$ powders were carefully mixed and milled in agate mortars. After being sintered at 1223 K in Ar atmosphere for 10 h, the calcined powders were remilled and pressed into pellets under 8 MPa, and then calcined at 1323 K in Ar atmosphere for 12 h into polycrystalline CuFe$_{1-x}$Cr$_x$O$_2$.

The crystallography of the synthesized CuFe$_{1-x}$Cr$_x$O$_2$ powders were characterized by Bruker D8 X-ray diffractometer (XRD) using Cu-Ka radiation. Raman spectroscopy was employed on a laser Raman spectrometer with an excitation wavelength of 532 nm. A field emission scanning electron microscope (FESEM, Quanta 250 FEG) coupled with energy dispersive spectroscopy (EDS) were used to observe the microstructure and to detect the composition of samples. The valence states of elements were detected by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi). Positron lifetime calculations were performed by using the atomic superposition (ATSUP) method in $3 \times 3 \times 1$ CuFeO$_2$ super-cell structure. The positron annihilation lifetime spectra (PALS) were measured at room temperature adapting a fast-fast coincidence lifetime spectrometer and the lifetime spectra were analyzed using the Positron Fit-extended program. The magnetic properties were investigated by a commercial physical property measurement system (Quantum Design-Dyna cool).

3. Results and discussion

3.1. Phase and structural characterization

Figure 1 shows the XRD patterns of CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0$–$0.4$) series at room temperature. All the diffraction peaks can be well indexed as a delafossite structure with R$3$m space group (PDF#01-085-0605), without any detectable secondary phase. Rietveld refinement of XRD data is carried out to obtain the lattice information. As an example, the Rietveld refinement of CuFe$_{0.5}$Cr$_{0.5}$O$_2$ sample is shown in Figure 1(b). Figure 1(c) displays the plot of the $a$ and $c$ values and the values decrease monotonously with increasing Cr$^{3+}$ content $x$, which is ascribed to the smaller ionic radius of Cr$^{3+}$ ($r_{\text{Cr}}^{3+} = 0.605$ Å) than that of Fe$^{3+}$ ($r_{\text{Fe}}^{3+} = 0.645$ Å). It should be noted that the $c/a$ ratio shown in Figure 1(d) increases with rising $x$, in spite of the reduction among both $a$ and $c$ values. This increment of $c/a$ ratio implicates a noticeable change occurring along the $a$-axis rather than that of $c$-axis. All these variations in lattice parameters along $a$- and $c$-axis accord with Vegard’s law and signify that Cr$^{3+}$ ions have successfully entered into the CuFeO$_2$ lattice sites and formed the homogeneous CuFe$_{1-x}$Cr$_x$O$_2$ solid solution.

Figure 2 shows Raman spectra of CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0$–$0.4$) specimens recorded at room temperature. Generally, the delafossite structure is characterized by rhombohedral symmetry with the point group $C_{3v}$, and the space group R$3$m, with four atoms in the primitive cell, which generates 12 optical phonons modes ($T_{\text{opt,R3}} = A_{1g} + E_g + 3A_{2u} + 3E_u$), and among them only $A_{1g}$ and $E_g$ symmetry are Raman active modes [29]. The former implies the vibration of Cu-O bond along the $c$-axis, while the latter represents movement in the triangular lattice perpendicular to the $c$-axis [29,30]. As is shown in Figure 2, the spectrum of CuFeO$_2$ displays two typical vibrational modes, which is consistent with other delafossite structure [31,32]. The two modes identified as $\sigma(A_{1g})$ at 685 cm$^{-1}$ and $\sigma(E_g)$ at 344 cm$^{-1}$ may be related to the spectral features of the O-Cu-O chain and edge-sharing FeO$_6$ octahedra, respectively. With increasing Cr$^{3+}$ content
From 0.0 to 0.4, the both active modes have a significant blue-shift, especially for $E_g$ mode, in line with the lattice contraction along the different axes, as confirmed by XRD results (Figure 1c), implicating an enhancement of (Fe, Cr)-O bonding. Meanwhile, the relative intensity of $E_g$ mode decreases conspicuously and the peak widens, which reflects that the amount of the molecular polarizability has been weakened and some disorder does arise in local of Fe$^{3+}$ grids. In addition, starting from $x = 0.1$, it also can be noted that a strong increase in intensity of the initially weak band around 513 cm$^{-1}$. The additional band is possibly
Figure 3. The SEM of CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0$–$0.4$) specimens and EDS elemental mapping (Cu, Fe) with elemental analysis report of $x = 0.4$ sample.

|  $x$  | C-K | O-K  | Cr-K | Fe-L | Cu-L |
|------|-----|------|------|------|------|
| 0.0  | 65  | 44.01| 9.96 | 18.02| 27.36|
| 0.1  |     |      |      |      |      |
| 0.2  |     |      |      |      |      |
| 0.3  |     |      |      |      |      |
| 0.4  |     |      |      |      |      |

**Figure 4.** XPS spectra of CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0$–$0.4$): (a) full-scale spectrum, (b) Cu-2p, (c) Fe-2p, and (d) Cr-2p peaks.
attributed to nonzero wave vector phonons which are commonly forbidden by Raman selection rules [30]. As mentioned, the selection rules may be relaxed by inherent defects such as Cu vacancies or interstitial oxygen [30].

### 3.2. Microscopic morphology characterization

Figure 3 shows the SEM images of CuFe$_{1-x}$Cr$_x$O$_2$ (x = 0.0–0.4) series. It can be seen that Cr$^{3+}$ doping exerts a distinct impact on the particle shape of CuFeO$_2$-based ceramics. The undoped CuFeO$_2$ is composed by some conterminous amorphous grains, attached to some crushed grains. This morphology displays abnormal growth and brisk grain boundary migration, indicating the presence of liquid phase sintering traces. In the CuFeO$_2$ system, copper oxide with low-melting can readily migrate to grain boundaries and thus cause abnormal morphologies characteristics. As Cr$^{3+}$ content x increases, the connected particles fragment gradually and form considerable fine grains. The EDS of x = 0.4 sample is shown in the lower right of Figure 3. The element percentages of Cu (27.36 at.%), Fe (18.02 at.%), Cr (9.96 at.%), and O atoms are almost homogeneously distributed and finally form a homogeneous CuFe$_{1-x}$Cr$_x$O$_2$ solid solution.

### 3.3. Compositional analysis

Figure 4(a–d) displays full-scale, Cu-2p, Fe-2p and Cr-2p spectra of CuFe$_{1-x}$Cr$_x$O$_2$ (x = 0.0–0.4) specimens, respectively. The full-scale spectrum confirms that only C, O, Cu and Fe elements are detected in primitive CuFeO$_2$ and additional Cr is detected in Cr$^{3+}$ doped CuFeO$_2$ sample. The typical Cu-2p spectra are exhibited in Figure 4(b), two distinct and intense binding energy peaks centered at 931.8 eV and 951.7 eV, are attributed to Cu 2p3/2 and Cu 2p1/2, respectively. No satellite peak can be observed, which confirms the occurrence of Cu in monovalent (+1) [33]. In case of the Fe-2p state, as shown in Figure 4(c), two intense peaks corresponding to Fe 2p3/2 and Fe 2p1/2 are observed at 710.6 eV and 724.1 eV, respectively. The binding energy distribution accords with FeO$_2$ in literature [34], which suggests the occurrence of Fe in trivalent (+3). In case of the Cr-2p state in Figure 4(d), two strong signals are located in the spectrum at 575.1 eV and 585.0 eV, corresponding to Cr 2p3/2 and Cr 2p1/2, respectively. The binding energies for Cr 2p3/2 of the Cr$^{3+}$ peak is located at 575.6 eV, and for Cr 2p1/2 of the Cr$^{2+}$ peak is assigned at 585.4 eV in literature [27]. The results manifest that the valence state of Cr is +3. Other valence states such as Cr$^{2+}$ and Cr$^{4+}$ are not observed in Cr-2p spectra. Therefore, it can conclude that the foreign Cr$^{3+}$ ions do not change the valence state of Cu$^{2+}$ and Fe$^{3+}$ in CuFeO$_2$.

### 3.4. PALS analysis

PALS is a useful and effective mean to detect the defects in solids [35]. When positrons are infused into a solid, they are readily captured and annihilated by electrons, thus forming two 511 keV γ quanta. The lattice and defect region in solid present distinctive electron density and distribution characteristics, respectively, and they would have different annihilation lifetimes. Therefore, PALS offer the annihilation information in lattice and defective region, which presents the characteristics of lattice and defect, such as the electrons density, defect type and defect concentration in solid qualitatively. According to multichannel positron trapping model, at least three independent components including three diverse lifetimes of positron (two for positron trapping and one for o-Ps decaying) as well as their corresponding intensities, which denote the quantity of defect can be acquired in the resolved PALS [36].

Cation vacancies are universally considered as the primary point defects in delafossite ABO$_2$ oxides and forcibly affect the material performance. Therefore, it is necessary to study the characteristics of vacancy defects in our current study. The ATSUP method in 3 × 3 × 1 super-cell structure are adopted to calculate the positron annihilation lifetime in the bulk and vacancy defect trapping states. Figure 5(a) shows the schematic diagram of perfect delafossite CuFeO$_2$ super-cell (3 × 3 × 1, including 108 atoms), and in which the Cu, Fe, and O atoms are denoted by blue, yellow and red balls, respectively. Figure 5(b–d) presents positron annihilation in bulk (V$_b$), single copper vacancy (V$_{Cu}$) and single iron vacancy (V$_{Fe}$), respectively. And the hollow represents positron wave function distribution at various defect states. In terms of theory calculation, the relevant theoretical lifetime values of primitive CuFeO$_2$ are calculated and listed in Table 1. Meanwhile, PALS is measured to probe the crystal defects in CuFe$_{1-x}$Cr$_x$O$_2$ ceramics in the present experiment. All spectra are resolved into τ$_{1}$, τ$_{2}$, and τ$_{3}$ and their relevant intensities I$_{1}$, I$_{2}$, and I$_{3}$ (I$_{1}$+I$_{2}$+I$_{3}$ = 1), in which τ$_{3}$ (1235–1750 ps) resulting from o-Ps annihilation on the sample surface is ignored in the following discussion for a negligible intensity (I$_{3}$ < 0.5%) [37]. According to the two-state trapping model [6,37], the τ$_{1}$ mostly represents the free-state annihilation characteristics for a perfect crystal lattice without any defects while the τ$_{2}$ denotes the captive state acting with the defects.

Table 2 lists the lifetimes and intensities with only two ingredients after normalizing I$_{1}$ and I$_{2}$. From Table 2, the τ$_{1}$ and τ$_{2}$ for primitive CuFeO$_2$ is 173.8 ps and 365.9 ps, respectively. In case of the τ$_{3}$, the values monotonously decrease as Cr$^{3+}$ content x increases. In view of τ$_{1}$, it can approximately reflect the lattice essence, the gradual decrease of τ$_{1}$
Figure 5. (a) The perfect crystal structure of CuFeO$_2$ super-cell ($3 \times 3 \times 1$, including 108 atoms). (b–d) Schematic diagram of positron annihilation in bulk, single copper vacancy ($V_{Cu}$) and single Fe vacancy ($V_{Fe}$), respectively. The Cu, Fe, and O atoms are denoted by blue, yellow and red balls.

Table 1. The relevant positron theoretical lifetime values: positron annihilation in bulk $V_b$, in single $V_{Cu}$, $V_{Fe}$, and in divacancies $V_{Fe-O}$, $V_{Cu-O}$ of primitive CuFeO$_2$.

| vacancy  | $V_b$ (ps) | $V_{Cu}$ (ps) | $V_{Fe}$ (ps) | $V_{Fe-O}$ (ps) | $V_{Cu-O}$ (ps) |
|---------|------------|---------------|---------------|-----------------|-----------------|
| Lifetime| 155.6 ps   | 197.4 ps      | 163.0 ps      | 177.7 ps        | 221.8 ps        |

Table 2. The positron annihilation parameters $\tau_1$, $\tau_2$, $I_1$, $I_2$, and $\tau_m$ of CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0–0.4$).

| sample              | $\tau_1$ (ps) | $\tau_2$ (ps) | $I_1$ (%) | $I_2$ (%) | $\tau_m$ (ps) |
|---------------------|---------------|---------------|-----------|-----------|---------------|
| CuFeO$_2$           | 173.8 ± 1.7   | 365.9 ± 11.8  | 84.4      | 15.5      | 203.4         |
| CuFe$_{0.5}$Cr$_{0.5}$O$_2$ | 172.9 ± 1.7   | 358.9 ± 11.3  | 83.1      | 16.8      | 203.9         |
| CuFe$_{0.75}$Cr$_{0.25}$O$_2$ | 170.0 ± 1.8   | 346.7 ± 11.3  | 82.7      | 17.2      | 200.9         |
| CuFe$_{0.25}$Cr$_{0.75}$O$_2$ | 169.3 ± 2.0   | 337.7 ± 11.1  | 80.5      | 19.4      | 201.8         |
| CuFe$_{0.5}$Cr$_{0.5}$O$_2$ | 166.5 ± 2.2   | 329.5 ± 11.2  | 79.1      | 20.8      | 200.2         |

Further indicates that Cr$^{3+}$ ions enter into the CuFeO$_2$ lattice and induce the local lattice contraction, which is in line with the XRD results (Figure 1c). Compared with the theoretical calculation results in Table 1, defect-annihilation lifetime $\tau_2$ (365.9 ps) far outclasses the theoretical calculation values: single $V_{Cu}$ (197.4 ps) and $V_{Fe}$ (163.0 ps) even divacancy $V_{Fe-O}$ (177.7 ps) and $V_{Cu-O}$ (221.8 ps), which indicates that the system defect not simply contains single vacancies or divacancies but vacancy clusters. For clarity, Figure 6 shows the defect-annihilation parameters $\tau_2$ and $I_2$ versus Cr$^{3+}$ content $x$. The $\tau_2$ monotonously decreases while the $I_2$ increases with increasing $x$. The decrease of $\tau_2$ and the increase of $I_2$ indicate that Cr$_2$O$_3$ with high melting point can effectively reduce the volume of cation vacancy group in CuFeO$_2$ lattice, but increase the vacancy concentration. The mean lifetime $\tau_m$ mainly reflects the total defect condition near the positron annihilation sites including the delocalized annihilation process in free and trapped states, which can be calculated in light of the formula [38]:

$$\tau_m = I_1 \tau_1 + I_2 \tau_2$$  \hspace{1cm} (1)

Noticeable, the $\tau_m$ (Table 2) varies in a small scale ($\Delta \tau_m < 4$ ps) within the entire dopant level, thus demonstrates that the chemical surroundings in annihilation sites inside the CuFeO$_2$ system remain basically unchanged [39].
3.5. Magnetic characterization

Figure 7(a) shows the zero-field-cooling (ZFC) curves of CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0–0.4$) compounds measured under the $H = 5$ kOe field. For clarity, the enlarged details of ZFC curves in 0–50 K are given in the inset of Figure 7(a). All the samples present the low temperature antiferromagnetic transition. For the primitive CuFeO$_2$ sample, similar to previous report [7,15], undergoes successive magnetic transitions from PM phase to partially disordered phase (quasi-long-range antiferromagnetic order) and then to 4SL $\uparrow\downarrow\uparrow\downarrow$ phase, as denoted by the $T_{N1}$ and $T_{N2}$, respectively. But for Cr$^{3+}$-doped samples ($x = 0.1$), interestingly, a broad bulge appears near 12 K denoted as $T_{N1}'$, and an emerging characteristic peak appears around 6 K denoted as $T_{N2}'$. The broad bulge may be due that the establishment of short-range order originating from order-by-disorder phenomenon destroys intrinsic magnetic order structure (quasi-long range antiferromagnetic order) [40]. And the emerging $T_{N2}'$ represents an exemplary antiferromagnetic transition peak which symbolizes the dominant long-range antiferromagnetic order between Fe-Fe or Cr-Cr. Noticeable, as the Fe$^{3+}$ contents are systematcially diluted by Cr$^{3+}$, the $T_{N1}'$ and $T_{N2}'$ both shift toward low values, which hints that Cr$^{3+}$ doping could suppress the antiferromagnetic transition temperature of CuFe$_{1-x}$Cr$_x$O$_2$ series obviously. To show more directly, the Curie-Weiss fit of the inverse molar susceptibility ($\chi^{-1}$) curves are given in Figure 7(b), presenting linear behavior at high temperature. The parameters including Curie constant $C$, Curie-Weiss temperature $T_\theta$, experimental effective moment
Table 3. Estimated Curie constant, Neel temperature $T_N$ and experimental effective moment $\mu_{\text{eff}}(\exp)$ and theoretical moment $\mu_{\text{eff}}(\text{th})$ in the high temperature paramagnetic region for CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0–0.4$) compounds.

| sample    | $C$  | $T_N$  | $\mu_{\text{eff}}(\exp)$ (μB) | $\mu_{\text{eff}}(\text{th})$ (μB) |
|-----------|------|--------|-------------------------------|-----------------------------------|
| CuFeO$_2$ | 4.0858 | $-97.33$ | 5.7170 | 5.91 |
| CuFe$_{0.7}$Cr$_{0.3}$O$_2$ | 3.6202 | $-90.64$ | 5.3815 | 5.74 |
| CuFe$_{0.6}$Cr$_{0.4}$O$_2$ | 3.3541 | $-89.40$ | 5.1800 | 5.56 |
| CuFe$_{0.5}$Cr$_{0.5}$O$_2$ | 3.1229 | $-94.28$ | 4.9983 | 5.38 |
| CuFe$_{0.4}$Cr$_{0.6}$O$_2$ | 3.1214 | $-106.92$ | 4.9971 | 5.19 |

$\mu_{\text{eff}}(\exp)$ and theoretical moment $\mu_{\text{eff}}(\text{th})$ are summarized in Table 3. Herein, the negative $T_N$ values indicate the predominant antiferromagnetic interactions and the obtained $\mu_{\text{eff}}(\exp)$ values dependent with Cr$^{3+}$ content $x$ are basically in line with the $\mu_{\text{eff}}(\text{th})$ [41]. As the Fe$^{3+}$ contents keep decreasing in CuFe$_{1-x}$Cr$_x$O$_2$, the downward deviation of the $\chi^{-1}$-$T$ curves from the Curie-Weiss fit is well strengthened. This trend hints the facilitation of Cr$^{3+}$ ions substituting on the short-range magnetic correlation of CuFe$_{1-x}$Cr$_x$O$_2$ series [42].

To further investigate the magnetization, the magnetization hysteresis ($M$-$H$) curves of CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0–0.4$) are measured at $T = 13$ K. As Figure 8 shows, an exemplary linear pattern manifested the predominant of antiferromagnetic behavior can be observed in all the samples. And the magnetization gradually improves with increasing Cr$^{3+}$ content $x$. The augment in magnetization is in accordance with the ZFC curves (Figure 7(a)), further indicating the enhanced short-range magnetic correlation in the Cr$^{3+}$-doped compounds. Meanwhile, it should be recalled that the $I_2$ (Figure 6) exhibits a similar trend to the magnetization. As Cr$^{3+}$ contents $x$ gradually increases, the native defect concentration increases. In the primitive CuFeO$_2$, two mechanisms contribute to the magnetism, i.e. the intra-layer exchange interaction by Fe-O-Fe pathways and the interlayer exchange interaction by Fe-O-Cu-O-Fe pathways [6]. Other than the changes of spin frustration arising from lattice distortion; therefore, the improvement in magnetization is also relevant to the redistributed cationic vacancies. The increasing Cr$^{3+}$ ions enlarge the defect concentrations, thus simplifying the long-range antiferromagnetic configuration and prompting the reinforcement of short-range magnetic correlation.

Given that the magnetization versus time ($M$-$t$) curves could well characterize the low temperature dynamic behavior and the short-range magnetic correlation [42,43], the $M$-$t$ curves of CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0–0.4$) samples are measured. As is shown in Figure 9, through zero-field cooling the samples to 5 K, applying a $H = 50$ kOe field and then turning off the field, the zero-field remanent magnetization versus time is recorded immediately. And for more intuitive comparation, the data are normalized by dividing $M_0$ ($M_0$ is equal to the magnetization at $t = 0$ moment) to remain the identical starting point. It can be seen that the magnetization of primitive CuFeO$_2$ hardly decays in the period of measurement, suggesting the unalterable magnetic ground state. The stationary magnetization is in line with the low-temperature 4SL $\uparrow\uparrow\downarrow\downarrow$ long-range antiferromagnetic order of Fe-O-Fe. But for Cr-doped samples, the magnetization presents a relaxation with time and the relaxation becomes rapider and rapider with increasing Cr$^{3+}$ content $x$. It can be recollected that the substitution of Cr$^{3+}$ for Fe$^{3+}$ ions contributes to the destruction of intrinsic magnetic structure and the formation of short-range

Figure 8. The $M$-$H$ curves for CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0–0.4$) measured at $T = 13$ K.
order. The results further demonstrate that the short-range magnetic correlation becomes more and more prevalent as Cr$^{3+}$ content $x$ increases. The prevailing short-range order is more easily to be driven by the thermal activation energy and thus be more quickly restored to equilibrium.

4. Conclusion

In conclusion, CuFe$_{1-x}$Cr$_x$O$_2$ ($x = 0.0–0.4$) compounds are synthesized successfully by direct solid-state reaction. The results reveal that Cr$^{3+}$ ions have successfully entered into the CuFeO$_2$ lattice sites but do not change the valance state of the Cu$^+$ and Fe$^{3+}$ ions. The bulk and vacancy-defect lifetimes are simulated by the ATSUP method in $3 \times 3 \times 1$ supercell structure. By comparing the theoretical and experimental results, the positrons of CuFeO$_2$ system are mainly annihilated in vacancy clusters. With increasing Cr$^{3+}$ content $x$, the open volume of vacancy defects decreases but the concentration of vacancy defects increases. However, the chemical surroundings in annihilation sites remain unchanged. Magnetization measurements results signify that the substitution of Cr$^{3+}$ can significantly destroy the inherent magnetic structure, reduce the antiferromagnetic transition temperature, and promote the formation of local short-range order. With the substitution of Cr$^{3+}$, the short-range order becomes more and more prevalent. The prevailing magnetic correlations are more easily determined by the thermal activation energy and a faster dynamic behavior is observed.

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The authors declare that they have no conflicts of interest.

Disclosure statement

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