J Supercond Nov Magn (2013) 26:2557–2559
DOI 10.1007/s10948-012-1726-7

ORIGINAL PAPER

Magnetization Study in $CuCr_2O_4$ Spinel Oxide

Thiago T. Gurgel · M.A. Buzinaro · N.O. Moreno

Received: 11 June 2012 / Accepted: 2 July 2012 / Published online: 20 July 2012
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Abstract We report magnetization and *ac* susceptibility as functions of the temperature and frequency for $CuCr_2O_4$ spinel oxide from 2 K to 300 K. Bulk $CuCr_2O_4$ crystallizes at room temperature in a tetragonal distorted spinel and above 865 K its structure is cubic spinel; distortion is caused by Jahn–Teller Cu^{2+} ions. The magnetization data of the polycrystalline sample indicates ferrimagnetic order below $T_C = 122$ K. Magnetization isotherm resulted in an average magnetic moment of 0.08 μ_B/f.u. at 2 K values lowest to expected value. This discrepancy can be explained assuming a triangular configuration of spins Cr^{3+} and Cu^{2+}. The ferromagnetic phase of the sample does not show glassy behavior. Its magnetic response can be explained simply from the domain wall dynamics of otherwise homogeneous ferrimagnet.

Keywords $CuCr_2O_4$ · Chromites · Ferrimagnetic ordering

1 Introduction

Complex oxides with spinel structure comprise a family of materials which exhibit a wide range of electronic, magnetic, and optical properties through the variation of cations on tetrahedrally and octahedrally coordinated sites [1]. Spinel ferrite, especially the chromite ACr_2O_4 (A = Co, Ni, Cu, Zn, etc.), has renewed research interest due to its applications in nanoscience and technology. Their physical properties depend upon the distribution of cations among the tetrahedral (A) and octahedral sites (B), and relative superexchange interactions via anions. The wide variety of cation substitutions can be made in tetrahedral sites (A) and octahedral (B) in the spinel network leading to a number of interesting physical properties, especially if the cation is magnetic [2, 3].

The main interest in studying the ACr_2O_4 spinel is to understand the role of the strongly negative J_{BB} (Cr–O–Cr) and J_{AB} (A–O–Cr) interactions in controlling the magnetic properties of chromites. In particular, $CuCr_2O_4$ is a normal spinel in which Cr^{3+} and Cu^{2+} ions are situated at the B and A sites, respectively. Copper chromite $CuCr_2O_4$ crystallize at room temperature in a tetragonal distorted (space group I41d) normal spinel crystal structure [4]. Above 865 K, its structure is a cubic spinel structure (space group Fd3m) and that distortion may be considered to arise because of a Jahn–Teller Cu^{2+} ions effect [5].

In this work, we study the oxide $CuCr_2O_4$ by dc/ac magnetization as a function of the temperature, frequency, and magnetic field.

2 Experimental Details

The polycrystalline samples of $CuCr_2O_4$ spinel oxide were prepared by the conventional solid state reaction. In this process, stoichiometric amounts of oxide CuO and Cr_2O_3, were weighed in the desired proportions, and then they were blended under acetone in an agate mortar and pestle with a grinding action for approximately 1 h. The calcination temperature was 1100 °C for 12 hours in a furnace with open atmosphere. The X-ray powder diffraction data were collected

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T.T. Gurgel (✉) · N.O. Moreno
Departamento de Física, Universidade Federal de Sergipe,
São Cristovão, SE 49100-000, Brazil
e-mail: thiagogto@gmail.com

M.A. Buzinaro
IFS, Av. Eng. Gentil Tavares da Mota, 1166, Aracaju,
SE 49045-60, Brazil

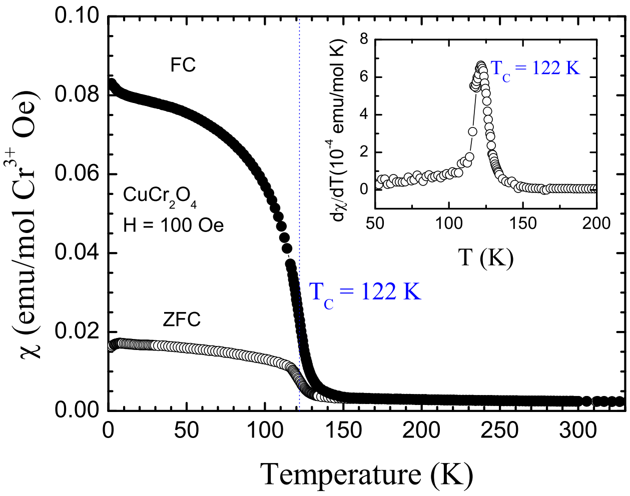

Fig. 1 Temperature dependence of dc magnetic susceptibility for $CuCr_2O_4$ measured in the ZFC (*open symbol*) and the FC (*solid symbol*) states with applied field of 100 Oe. The *inset* displays the first derivative os susceptibility of $CuCr_2O_4$

at room temperature using a Dmax2500 Rigaku diffractometer with radiation CuK_α ($\lambda = 1.5418$ Å). The magnetic measurements were made on commercial magnetometer MPMS (of Quantum Design) with SQUID detection operating in temperature range $2 \le T \le 300$ K and external magnetic field $0 \le H \le 7$ T.

3 Results

The X-ray powder diffraction pattern was indexed by assuming tetragonal symmetry (space group I41/*amd*). The XRD spectrum, did not show any additional phase; the bulk sample is single phase spinel structure. The lattice parameters obtained by least squares refinement of powder data are $a = b = 6.031$ Å and $c = 7.781$ Å in agreement with reported values [6].

In zero-field-cooled (ZFC) procedure, the magnetic field was turned to zero, and the temperature decreased from room temperature to 2 K. Then a magnetic field was applied to the sample and the magnetization M collected. On the other hand, the field-cooled (FC) procedure was done on cooling from sufficiently room temperature after M at ZFC was measured.

Figure 1(a) presents the dc magnetic susceptibility (χ) for $CuCr_2O_4$ as a function of the temperature in an applied magnetic field of 100 Oe. The ZFC and FC curves, show the behavior of a typical ferrimagnet, where the susceptibility decreases with increasing temperature up to T_C wherein the ferrimagnetic order breaks down.

The bifurcation between the ZFC and the FC is due the movement of the magnetic domain walls or the difference arises from magnetocrystalline anisotropy instead of the that expected of a spin-glass-like transition [7]. Measured in the ZFC state, the domain structure at low temperatures differs from that at high temperatures, and the domain structure is adjusted from the low-temperature to the high-temperature one by gradually increasing the temperature. As measured in the FC state, the domain retains the high-temperature configuration from 2 to 300 K. When a strong magnetic field is applied, the ZFC and FC curves collapse displaying irreversibility. The ordering temperature ($T_C \simeq 122$ K) was defined as the temperature where $d\chi/dT$ has a maximum (inset Fig. 1, which is in good agreement with the bulk value of 135 K [8, 9]).

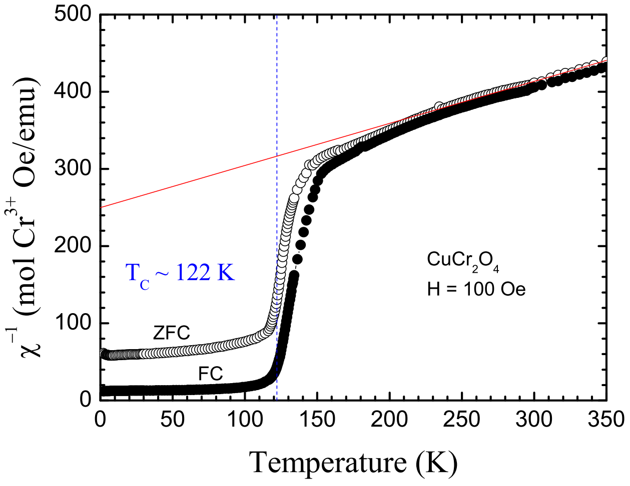

Fig. 2 Temperature dependence of inverse of magnetic susceptibility for $CuCr_2O_4$. *Solid line* represents the Curie–Weiss fitting

Figure 2 shows the temperature dependence of the inverse of magnetic susceptibility for the $CuCr_2O_4$ chromite. χ^{-1} follows the hyperbolic behavior characteristic of ferrimagnets [10]. The solid line is a fit of the χ^{-1} data using the Curie–Weiss law. The asymptotic paramagnetic Curie temperature obtained by extrapolation of this straight line to the T-axis gives $\theta = -450$ K.

Figure 3 shows the frequency dependence of real part χ_{ac} of *ac* susceptibility. The temperature variation of χ_{ac} shows paramagnetic to ferromagnetic transition around 122 K followed by a hump. There is no shift in temperatures of the peaks with frequency for real and imaginary part.

The frequency independence of the magnetic transitions in both compounds shows small amounts of disorder in these samples. These measurements provide further evidence for coexisting ferrimagnetic and anti-ferromagnetic regions in the mixed composition compounds.

In Fig. 4, we show the field (H) dependence of magnetization (M) at 2, 130, and 300 K. The isotherms at 2 K indicate a typical ferrimagnetic nature the sample, characterized by a sharp increase of M to achieve the saturation level above 10 kOe. The saturated magnetic moment (M_S) of the $CuCr_2O_4$ was estimated from the linear extrapolation

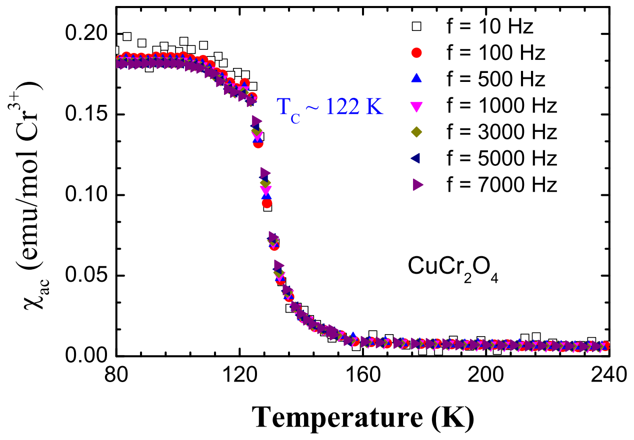

Fig. 3 Temperature dependence of real part of *ac* susceptibility for $CuCr_2O_4$ at different frequencies

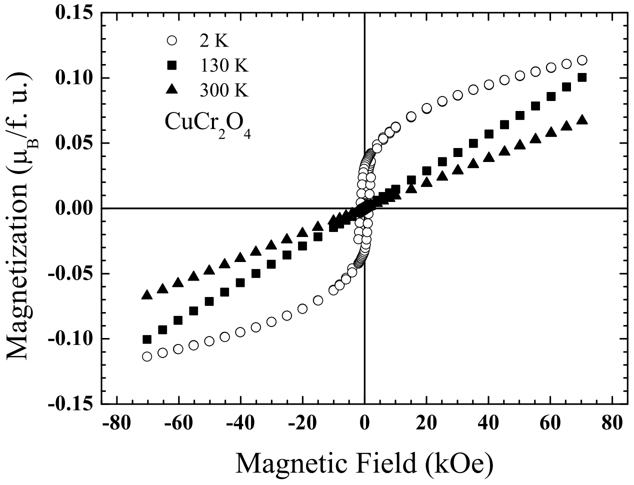

Fig. 4 Field dependence of magnetization for $CuCr_2O_4$ at 2 K, 130 K, and 300 K

of high field $M(H)$ data to intersect on M axis at $H = 0$ value. Resulted in an average magnetic moment of 0.080 μ_B per formula unit at 2 K which is rather less than the bulk values (0.5–0.8 μ_B/f.u.) and coercive field of about 2.0 kOe. While at temperatures of 130 K and 300 K, a linear behavior of M vs. H curves is observed, ascribed to the paramagnetic regime. At 2 K, $CuCr_2O_4$ has a coercive field of about 2.0 kOe and a saturation moment of 0.08 μ_B/f.u. per formula unit. The Néel model of antiferromagnetism predicts a saturation moment of 5 μ_B/f.u. per formula unit in $CuCr_2O_4$. The low moment is due to the triangular arrangement of spins, the Cu^{2+} sublattice couples anti-ferromagnetically to the net moment of the Cr^{3+} sublattices creating a triangular configuration of spins.

4 Conclusions

The $CuCr_2O_4$ was successfully prepared by the solid state method and calcinate at 1100 °C for 12 hours. The X-ray diffraction studies clearly show the formation of single phase spinel structure. The saturated average magnetic moment of 0.08 μ_B/f.u. at 2 K is due to a non-collinear ferrimagnetic structure of copper chromite. The ferrimagnetic phase of the sample does not show glassy behavior as seen in other chromite spinels with geometrical frustration.

Acknowledgements The authors wish to thank the Brazilian funding agencies CNPq, CAPES, and FAPITEC/SE for financial support.

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