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Study of magnetic entropy and ESR in ferromagnet $CuCr_2Te_4$

Renwen Li [a,b], Changjin Zhang [a,*], Yuheng Zhang [a]

[a] High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[b] Department of Physics and Electronic Engineering, Hefei Normal University, Hefei 230061, People's Republic of China

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ABSTRACT

The magnetic entropy around the critical temperature (T_C) has been systematically investigated in $CuCr_2Te_4$. Reliable critical exponents β, γ and δ are obtained according to the magnetic field (H) dependence of magnetic entropy (S_M) change $|\Delta S_M|^{max} \propto H^n$ with $n=(1+(1/\delta))(1-(1/\beta))$ and modified Arrott plot method. The critical exponents are found to obey the single scaling equation of $M(H,\varepsilon)=\varepsilon^{\beta} f_{\pm}(H/\varepsilon^{\beta+\gamma})$, where $f_{\pm}$ is regular functions with f_{+} for $T>T_C$, f_{-} for $T<T_C$, ε is the reduced temperature $(T-T_C)/T_C$. It proves that the magnetic field dependence of magnetic entropy change is an effective and valid method to study the critical behavior in this kind of ferromagnet. Detailed analysis of the electron spin resonance experiment reveals that a strong spin–orbit coupling arises near T_C in $CuCr_2Te_4$. This strong spin–orbit coupling may have a significant effect on the deviation of the exponents.

1. Introduction

Recently, chromium-based spinel chalcogenides $CuCr_2X_4$ (X=S, Se and Te) have attracted considerable interests due to their amusing properties including the pronounced room-temperature magneto–optic Kerr effect [1] and the anomalous Hall effect [2–4], etc. This kind of material has also been theoretically predicted to be highly spin-polarized [5], which makes them potential materials for spin-based electronic devices. To explain the peculiar ferromagnetism (FM) and metallic conduction, Lotgering and van Stapele [6,7] have proposed a ferromagnetic-hybridized electronic configuration $Cu^{1+}Cr^{3+}_{\uparrow}X^{1-}_{\downarrow}Cr^{3+}_{\uparrow}X^{2-}_{3}$ (X=S, Se and Te), where they attributed the FM and the conductivity to the indirect coupling of the Cr spins via the holes in a ligand non-bonding X p–Cu d orbits. This configuration has been proved valid by various theoretic calculation and experiments, such as the density functional calculations, magneto–optical study, magnetic and transport study [1,8–11], etc. $CuCr_2Te_4$ is a typical compound in the FM metal spinel chalcogenides family. It possesses a FM metal ground state with the Curie temperature (T_C) as high as 326 K. In our previous work [12], based on the Kouvel–Fisher (K-F) method and critical isotherm analysis, we have obtained the critical exponents of $\beta=0.369\pm0.001$, $\gamma=1.27\pm0.01$, $\delta=4.73\pm0.01$ and the critical temperature $T_C=326.0\pm0.1$ K for ferromagnet $CuCr_2Te_4$.

Generally, the traditional method to investigate the critical behavior and to get the critical exponents depends on the fitting parameters in the Arrott–Nakes equation of state $(H/M)^{1/\gamma}=(T-T_C)/T_C+(M/M_1)^{1/\beta}$ [13], where M_1 is the material constant. Because of the uncertainty of the parameters, researchers usually have to try different theoretical models, such as 3D-Heisenberg ($\beta=0.365$), mean-field ($\beta=0.5$), 3D-Ising model ($\beta=0.325$) and tricritical mean field model ($\beta=0.25$), to first delineate some trial Arrott plots and then choose the best one to describe the critical behavior [14–16]. However, in practical operation, different models and fitting ranges may yield different critical exponents. Thus, a considerable deviation or uncertainty is unavoidable. It is known that the magnetic entropy change is an effective method to investigate the physical properties of a ferromagnet. Franco et al. and Halder et al. [17–19,20] have studied the critical behaviors in amorphous alloys, such as $Fe_{83}Zr_6B_{10}Cu$, $Gd_5Si_2Ge_{1.9}X_{0.1}$ (X=Al, Cu, Ga, Mn, Fe and Co), $Er_{1-x}Dy_xAl_2$ and $Mn_4FeGe_{3-x}Si_x$ series. They have proved that the magnetic field dependence of magnetic entropy change is an effective and valid method to determine the critical exponents of the soft magnetic amorphous alloys. However, this method is rarely applied and tested in the compounds like oxides and chalcogenides ferromagnets, etc. In this paper, we calculate the magnetic entropy of $CuCr_2Te_4$ chalcogenide ferromagnet and investigate its critical behavior based on the magnetic field dependence of the magnetic entropy change method. It is found that this method in studying the critical property of this kind of material is reliable and can be popularized to similar system. Detailed analysis of the electron spin resonance (ESR) experiment reveals that a strong spin–orbit coupling arises around critical

* Corresponding author. Tel.: +86 5515595655; fax: +86 5515591149.
E-mail address: zhangcj@hmfl.ac.cn (C. Zhang).

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temperature in $CuCr_2Te_4$. This strong spin–orbit coupling originates from the ligand non-bonding in Te p–Cu d orbits and may be responsible for the deviation of the critical exponents.

2. Experiment

Polycrystalline sample of $CuCr_2Te_4$ was prepared using the conventional solid-state reaction method described elsewhere [12]. The phase purity is confirmed by the powder X-ray diffraction (XRD). The magnetic measurement was performed with a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS 7T-XL). The sample was processed into ellipsoid shape and the applied field was put along the long axis. The isothermal magnetization was performed after the sample was heated well above the Curie temperature T_C for enough time to ensure that all curves were initial magnetizing. The electron spin resonance spectra were collected with a Bruker EMX plus model spectrometer at 9.32 GHz.

3. Results and discussion

Fig. 1(a) (left axes) shows the temperature dependence of magnetization (M–T) after zero-field-cooling (ZFC) sequence under the magnetic field $H=0.005$ T and 1 T, respectively. A sharp paramagnetic to ferromagnetic (PM–FM) phase transition occurs at $T_C \approx 326$ K defined by the peak in temperature dependence of the differential quotient of magnetization (dM/dT–T) under a low field of 0.005 T. As one can see that, under a higher external magnetic field of 1 T, the peak in dM/dT–T shifts to about 338 K. This is consistent with previous report [21].

According to Maxwell's relation, the isothermal magnetic entropy changes can be concluded as [22]

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH \quad (1)$$

Experimentally, the magnetic entropy change ΔS_M can be calculated through the isothermal M–H curves measured at temperatures with small temperature intervals and the absolute magnetic entropy change $|\Delta S_M|$ can be expressed as

$$|\Delta S_M| = -\Delta S_M \quad (2)$$

Thus the absolute magnetic entropy change $|\Delta S_M|$ was calculated at temperatures near the critical point with the applied magnetic field variation from 0.02 to 3 T. The left inset of Fig. 1(b) shows a typical $|\Delta S_M|$–T curve with 0.2 T magnetic field variation. According to the mean field theory, the relation between the magnetic entropy and the applied magnetic field variation near the magnetic phase transition is described as [23]

$$|\Delta S_M|^{max} \cong 1.07qR\left(\frac{g\mu_B JH}{kT_C}\right)^{2/3} \quad (3)$$

where q is the number of magnetic ions, R is the universal gas constant and g is the Lande g-factor. Obviously, $|\Delta S_M|^{max}$ should be proportional to H^n with $n=2/3$. However, the studies in the soft magnetic amorphous alloys [18,20] show that, $n=1$ well below T_C, $n=2$ well above T_C in the PM range, $n \approx 0.75$ at T_C. That is to say, experimentally determined value of n often deviates from 2/3. For this reason, Franco et al. [24] have suggested a new relation which agrees better with the experimental data:

$$n = 1 + \frac{1}{\delta}\left(1 - \frac{1}{\beta}\right) \quad (4)$$

where δ is the third exponent associated with critical magnetization isotherm at T_C. The δ value can be determined by $M_{T_C} = DH^{1/\delta}$ at critical point T_C, where D is the critical amplitude. As shown in the left inset of Fig. 1(b), $|\Delta S_M|$ reaches the maximum $|\Delta S_M|^{max}$ at T_C, and the value of $|\Delta S_M|^{max}$ is H dependent. By fitting the $|\Delta S_M|^{max}$–H curve in Fig. 1(b) we get $n=0.664 \pm 0.004$. Based on Eq. (4) and δ in critical isotherm analysis at 326 K, we get $\beta=0.383$, which agrees well with $\beta=0.369$ in the K–F method. Generally, the relative cooling power (RCP) for a material with magnetocaloric effect can be defined as [25]: $RCP = |\Delta S_M|^{max} \times \delta T_{FWHM}$, where δT_{FWHM} is the full width at half maximum of $|\Delta S_M(T)|$ curve. As plotted in the right inset of Fig. 1(b), according to Ref. [24], the RCP does yield linear dependence of $H^{1+(1/\delta)}$ with $\delta=4.73$ from critical isotherm analysis. These results indicate the reliability of the magnetic field dependence of magnetic entropy change in studying the critical behavior in the $CuCr_2Te_4$ system.

As a confirmation, the critical exponents are tested according to the scaling hypothesis. In the critical region, the magnetic equation can be written as [26]

$$M(H,\varepsilon) = \varepsilon^{\beta} f_{\pm}(H/\varepsilon^{\beta+\gamma}) \quad (5)$$

where $f_{\pm}$ is the regular functions with f_+ for $T > T_C$, while f_- for $T < T_C$, ε is the reduced temperature $(T-T_C)/T_C$. According to Eq. (5), the $M(H,\varepsilon)\varepsilon^{-\beta} \sim H\varepsilon^{-(\beta+\gamma)}$ relation should yield two universal curves for $T > T_C$ and $T < T_C$, respectively. As shown in Fig. 2(a), the isothemal magnetization data around T_C do collapse into two different curves, one above T_C and the other below T_C, which nicely obeys the scaling theory, indicating the reliability of the exponents.

We also use the Modified Arrott plot method to deduce the critical exponents for comparison with those from the K–F

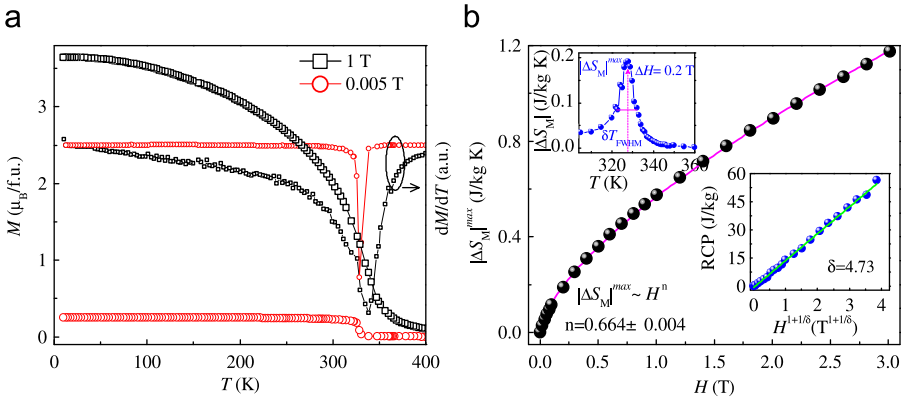

Fig. 1. (a) Temperature dependence of magnetization (left axis) and dM/dT (right axis) under 0.005 T and 1 T field for $CuCr_2Te_4$; (b) the H dependence of maximal absolute magnetic entropy change $|\Delta S_M|^{max}$ (the solid curve is fitted; the left inset shows $|\Delta S_M|^{max}$–T with 0.2 T magnetic field variation; the right inset shows the fitting and experimental data of $RCP \sim H^{1+(1/\delta)}$).