Critical behavior of the spinel $CdCr_2S_4$

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We present our investigation on the critical behavior of the spinel compound $CdCr_2S_4$ via the ac susceptibility and dc magnetization measurements. The analysis of ac susceptibility in terms of scaling behavior yields exponent values of $\delta=5.38\pm0.01$, $\gamma+\beta=1.77\pm0.03$ and $\gamma=1.44\pm0.02$. Both δ and γ are slightly larger than that predicted by Heisenberg model. Detailed analyses of the inverse of the susceptibility and the electron spin resonance experiment reveal that the existence of correlated magnetic polarons has a key impact on the ferromagnetism of the spinel $CdCr_2S_4$. The abnormal critical exponent value of δ of $CdCr_2S_4$ may be attributed to the formation of the correlated magnetic polarons and abnormal spin-phonon coupling. © *2009 American Institute of Physics*. [doi:10.1063/1.3269701]

I. INTRODUCTION

The chalcogenide spinel compounds ACr_2X_4 (A =Zn, Cd, Hg; X=O, S, Se) have attracted special interest in the past several years because a variety of important physical effects have been found in these compounds, such as colossal magnetoresistance (CMR), colossal magnetocapacitance (MC), etc.[1–4] Due to the strong coupling among spin, charge, and lattice degrees of freedom, this system shows not only interesting phenomena but also complicated magnetic structures.[5,6]

$CdCr_2S_4$ is a typical example that exhibits the second-order paramagnetic-ferromagnetic (PM-FM) transition at Curie temperature $T_C=84$ K (Curie–Weiss temperature $\Theta_{CW}=155$ K).[3] The spinel $CdCr_2S_4$ also displays the CMR effects. Recently, relaxor ferroelectricity and colossal magnetocapacitive effect have been reported for $CdCr_2S_4$.[1,2] The infrared and Raman scattering experiments also provide evidence of abnormal coupling between the spin and phonon well above the magnetic ordering temperature.[5–7] Electron spin resonance (ESR) measurements show that there exists a strong magnetic correlation among the polarons in $CdCr_2S_4$, which is different from a pure magnetic polaron system.[8] All of these interesting results reveal that there exists strong spin-phonon and spin-charge couplings in $CdCr_2S_4$. Therefore, relaxation effects, local polar distortions and the variations in the electronic states may play important roles in the MC and CMR effects in $CdCr_2S_4$. It is well known that the critical exponents might reflect information about the magnetic interactions around the phase transition temperature. A comprehensive study of the critical phenomenon of $CdCr_2S_4$ might be helpful in understanding the interesting magnetic and electronic properties of $CdCr_2S_4$. In this paper, the critical behavior in spinel compound $CdCr_2S_4$ is investigated via the detailed measurements of the ac susceptibility and dc magnetization.

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II. EXPERIMENT

The polycrystalline samples of $CdCr_2S_4$ were prepared by the standard solid-state synthesis method. The details of the sample preparations and their characterizations by the x-ray diffraction and magnetization measurements have been reported in Ref. 8. The magnetic measurements were carried out with a quantum design superconducting quantum interference device magnetic property measurement system ($1.8\ \mathrm{K}\leq T\leq 400$ K, $0\ \mathrm{T}\leq H\leq 5$ T). The measured samples were machined into cylinders 6 mm long and 1 mm diameter, and the applied field was parallel to the longest semiaxis of the samples. So the field could exist throughout the samples and the shape demagnetizing fields could be reduced as much as possible.

III. RESULT AND DISCUSSION

It is well known that the field- and temperature-dependent ac susceptibility measurements provide a powerful technology for the investigation of the continuous/second-order PM to FM phase transition.[9,10] The field dependence of the ac susceptibility, $\chi_m(H,t_m)$, shows a series of peaks which decrease in amplitude and increase in temperature as the applied field increases. These maxima are a signature of a continuous or second-order PM to FM transition. According to the scaling theory,[11,12] the locus in temperature, t_m, together with such maxima are governed by a set of power laws as follows:

$$t_m=(T_m-T_C)/T_C \propto H_i^{1/(\gamma+\beta)}, \tag{1}$$

$$\chi_m \propto t_m^{-\gamma}, \tag{2}$$

$$\chi_m \propto H_i^{(1-\delta)/\delta}, \tag{3}$$

where H_i is the internal field ($H_i=H_a-NM$, where N is the demagnetization factor and M, the associated magnetization). Figure 1 shows the ac susceptibility measured in various static biasing fields H_a. The Heisenberg model is used to find a quantitative estimate of T_C using the data above in

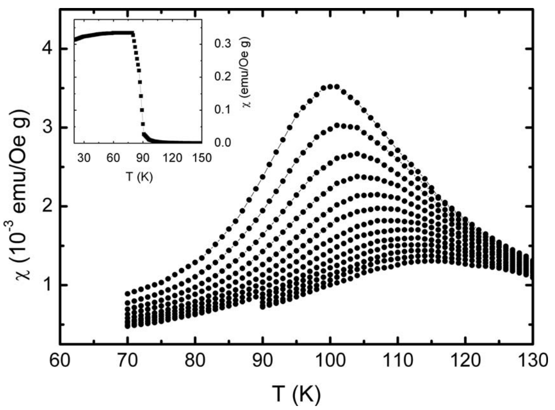

FIG. 1. ac susceptibility measured on warming following zero-field cooling in different static field from 10 kOe (top) to 34 kOe (bottom) in 2000 Oe steps. The inset shows the zero-field ac susceptibility (measured on warming).

conjunction with Eq. (1), i.e., by plotting the measured peak temperature T_m against the internal field $H_i^{0.57}$ using the Heisenberg model's prediction of $(\gamma+\beta)^{-1}=0.57$. The straight line dependence of T_m on H_i is plotted in the Fig. 2(a), the extrapolation of this line to $H_i=0$ yields an estimated T_C of

$$T_C = 85.6 \pm 0.3 \text{ K}.$$

Figure 2(b) shows the double-logarithmic plot of the critical peak susceptibility, $\chi_m(H,t_m)$ versus the internal field, H_i (with the demagnetizing factor N estimated from the maximum in the zero-field ac susceptibility), and confirms the power-law dependence, with the slope of this plot being $\delta = 5.38 \pm 0.01$. This estimation is independent of the choice of T_C and is used in the double-logarithmic plots of Fig. 2(c) and 2(b), in which the power law tests of the dependence of the (reduced) peak temperature, and the peak amplitude on the internal field are implied in Eqs. (2) and (3), respectively. These plots confirm such a power-low dependence and their slopes are $(\gamma+\beta)=1.77\pm0.03$ and $\gamma=1.44\pm0.02$ from which one gets $\beta=0.33\pm0.005$. These estimations of γ and δ are slightly larger than the Heisenberg model predictions [$\gamma=1.387$, $\beta=0.365$, $\delta=4.783$];[12] However, the exponent values obtained above obey the Widom relation $\gamma=\beta(\delta-1)$ within experimental uncertainty, which implies that the obtained β and γ values are reliable.[9] The value of γ is close to 1.36 ± 0.02 obtained from the dc magnetization[13] and 1.41 reported recently by Loidl group.[14]

In order to confirm these exponents, the estimation is provided by the ac susceptibility data. Figure 3(a) shows the data collected along the critical isotherms ($T_C=85.6$ K) obtained from the dc magnetization data. From the inset of Fig. 3(a), the evaluated δ is obtained according to the following equation:

$$M(H,T=T_C) = M_0 H^{1/\delta}. \tag{4}$$

The straight line fitting yields $\delta=5.52\pm0.11$, which is close to the estimated value obtained from the ac susceptibility data within the experimental uncertainty. However, the latter is independent of T_C. The above result also demonstrates that the critical values obtained from the ac susceptibility data are reliable. Our data are also compared with the prediction of

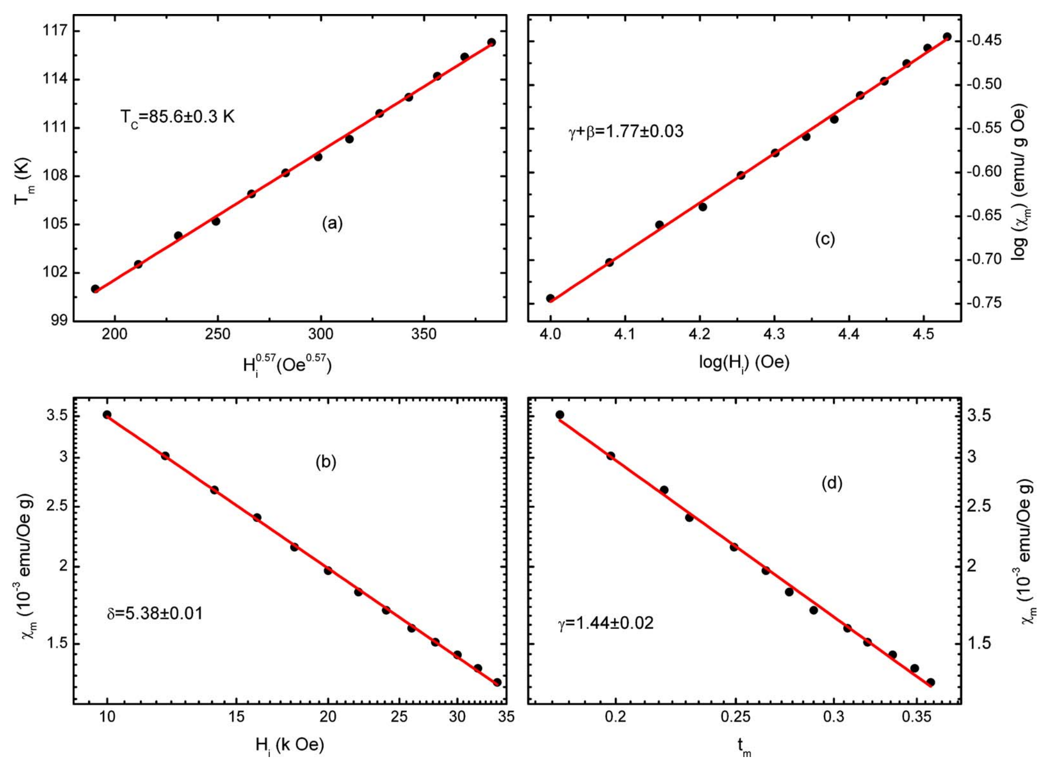

FIG. 2. (Color online) (a) Estimate of critical temperature T_C by plotting the susceptibility peak temperature (T_m) against ($H_i^{0.57}$). (b) The peak susceptibility, χ_m, taken from Fig. 1, plotted against the internal, H_i, on a double-logarithmic scale. The solid line confirms the power law, Eq. (3) and its slope yields δ. (c) A double-logarithmic plot of the reduced peak temperature, t_m, using the T_C estimate from Fig. 2(a), against the internal field (H_i). (d) The peak susceptibility, χ_m, taken from Fig. 1, plotted against the reduced temperature on a double-logarithmic scale.

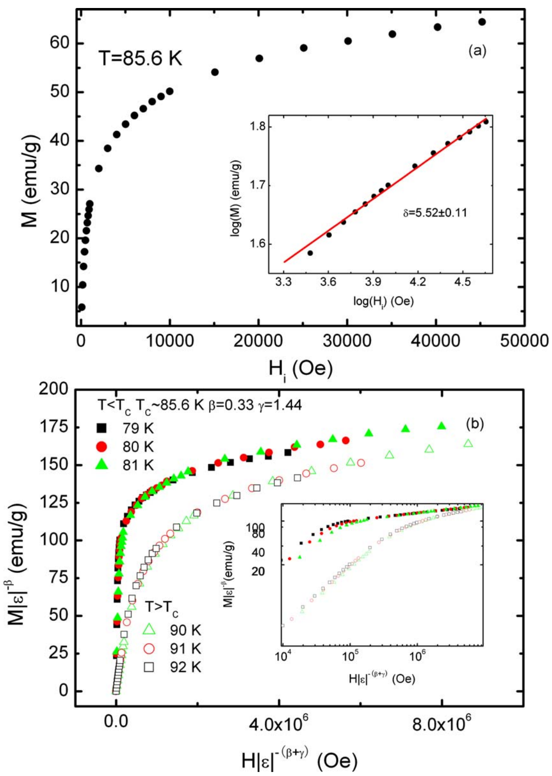

FIG. 3. (Color online) (a) dc magnetization measured along the critical isotherm (T_C=85.6 K), the inset shows the plot for determining the critical exponents δ. (b) Scaling plots for $CdCr_2S_4$ below and above T_C using β =1.44 and γ=0.33. The inset shows the same plots on log-log scale.

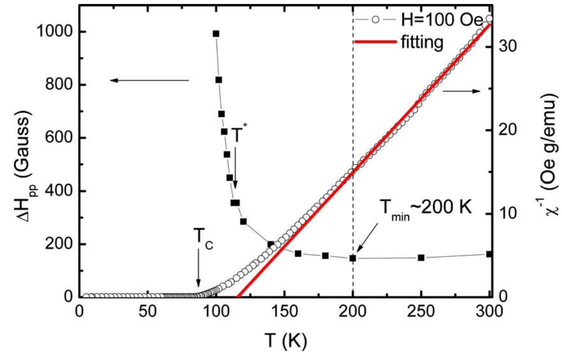

FIG. 4. (Color online) The temperature dependence of the inverse of magnetic susceptibility under a magnetic field of 100 Oe in the field cooled mode and ΔH_{pp} for $CdCr_2S_4$. T_{min} denotes the temperature where ΔH_{pp} is minimum and the inverse magnetic susceptibility deviates from the Curie–Weiss law. T^* corresponds to the temperature below which the distortion of line occurs.

the scaling theory. In the critical region, the magnetic equation of state is given by

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

where f_+ for $T>T_C$ and f_- for $T<T_C$ are regular analytical functions. $M/|\varepsilon|^{\beta}$ as a function of $H/|\varepsilon|^{-(\beta+\gamma)}$ produces two universal curves: one for temperatures below T_C and the other for temperatures above T_C. Using the values of β, γ, and T_C obtained from the ac susceptibility data, the scaled data are plotted in Fig. 3(b). The inset of Fig. 3(b) shows the same plots in log-log scale. All the points fall on the two curves, one for $T<T_C$ and the other for $T>T_C$. This suggests that the values of the exponents and T_C obtained from the ac susceptibility data are reasonably accurate.

In order to investigate the abnormal critical behavior present in our studied system $CdCr_2S_4$, the ESR experiment was carried out in our reported Ref. 8, the data are not shown in present paper. Temperature dependence of the peak-to-peak line width ΔH_{pp} is plotted in Fig. 4. At high temperatures, each spectrum consists of a single line with a Lorentzian line shape, which holds up to the temperature of T^* ~113 K. Some distortions occur and the resonance line greatly broadens below T^*. T^* corresponds to the temperature where the magnetic polarons become correlated in $CdCr_2S_4$. In order to study the spin interaction in $CdCr_2S_4$, the temperature dependence of the peak-to-peak line width ΔH_{pp} obtained from the ESR experiment is plotted in Fig. 4. The linewidth is directly connected to the interaction between the spins and their environment and to the spin motion.[15] From Fig. 4, it is found that, ΔH_{pp} decreases almost linearly with the decrease in the temperature and exhibits a minimum at the temperature T_{min} that is much higher than T^*. In order to compare the data obtained from the ESR with the inverse magnetic susceptibility, both ΔH_{pp} and χ^{-1} are plotted in the same temperature range. The fitting (solid line) is made according to CW law in the temperature range from 230 to 300 K. When the fitting is extrapolated to low temperatures, it is found that the fitting deviates from the straight line at 200 K, which is very close to the T_{min} values determined from ΔH_{pp}. It should be pointed out that such upward deviations are common in conventional ferromagnet. However, in our case, the temperature of the ΔH_{pp} minimum is in good agreement with the temperature where the fitting deviates from CW, implying that there exist some correlation between the minimum of ΔH_{pp} and the deviation from CW. From the reported results, the magnetic polarons first form a gas of magnetic polarons at temperature below T_{min}, and then transform into correlated polarons at T^*.[13] The existence of magnetic polarons affects the ferromagnetism in $CdCr_2S_4$.

Let us turn to the ac susceptibility data where the critical exponents are obtained, it is found that all ac susceptibility peak temperatures (T_m) do not excess the temperature T^*. In other words, the above critical behavior might reveal some information about correlated magnetic polarons system. For an inhomogeneous system, the magnetic polarons are no longer isolated, and magnetic correlation may exist. From this point, the magnetic polaron could be viewed as an island of local FM order in a PM host which is similar to the FM cluster existing in the some doped manganites where the Griffiths phase (GP) is present, which might be the reason why the critical behavior of $CdCr_2S_4$ is analogous to some manganites where the GP is present.[16] However, the concept of magnetic polaron differs from that of FM clusters. The former contains only one carrier and is regularly spaced and the latter may contain several carriers and has fractal shape.[17] On the other hand, the strong spin-lattice coupling should also be considered in the abnormal critical behavior of $CdCr_2S_4$.[4–6] In any case, to explore the magnetic and electronic mechanism of $CdCr_2S_4$, more experimental studies on high purity single crystal samples are required. Although the critical exponents could not supply the micromagneticstructure of $CdCr_2S_4$, the above findings provide a point of reference as well as an understanding of the anomalous behavior in some of the spinels with unconventional PM-FM transitions.

IV. SUMMARY

The critical behavior of the spinel compound $CdCr_2S_4$ is studied by the detailed measurements of the ac susceptibility and dc magnetization. The ac susceptibility in terms of scaling behavior yields exponent values of $\delta=5.38\pm0.01$ and $\gamma=1.44\pm0.02$ which are slightly larger than those predicted by Heisenberg model with $\beta=0.33\pm0.005$ and Curie temperature $T_C=85.6\pm0.3$ K. Detail analyses of the inverse of the susceptibility and the ESR experiment reveal that the existence of the correlated magnetic polaron has a crucial impact on the ferromagnetism of the spinel $CdCr_2S_4$. The abnormal critical exponent value of δ of $CdCr_2S_4$ can be owing to the formation of correlated magnetic polarons and abnormal spin-phonon coupling.

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