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Critical behavior of spinel vanadate $MnV_{1.95}Al_{0.05}O_4$

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ABSTRACT

The critical properties of the spinel vanadate $MnV_{1.95}Al_{0.05}O_4$ have been investigated by the Kouvel–Fisher method, and critical isotherm analysis. Reliable critical exponents $\beta=0.492(3)$, $\gamma=0.969(1)$ and $\delta=2.951(4)$ are obtained. Based on these critical exponents, the magnetization-field–temperature data around T_C collapse into two independent curves obeying the single scaling equation $M(H,\varepsilon)=\varepsilon^{\beta}f_{\pm}(H/\varepsilon^{\beta+\gamma})$. Moreover, the critical exponents are confirmed by the field dependence of the magnetic entropy change relation $\Delta S_M|_{T=T_C}\propto H^n$ with $n=1+(\beta+1)/(\beta+\gamma)$. The critical behavior of $MnV_{1.95}Al_{0.05}O_4$ agrees with the prediction of the mean-field model with long range interaction. Compared with MnV_2O_4, the different critical behavior of $MnV_{1.95}Al_{0.05}O_4$ might be because the doped Al ions destroy the collective frustration interaction between V ions. The ferromagnetism of $MnV_{1.95}Al_{0.05}O_4$ is mainly related to the long range ferromagnetic interaction of Mn ions.

1. Introduction

The spinel vanadium compounds AV_2O_4 (A=Zn, Mn, Mg and Cd) have attracted special interest in the past several years because a variety of important physical effects have been found in these compounds, such as orbital order (OO), ferroelectric effect and magnetocaloric effect [1–12]. Due to the strong coupling among spin, orbital and lattice degrees of freedom, this system shows not only interesting phenomena but also complicated magnetic structures.

MnV_2O_4 is a typical example that shows the second-order paramagnetic–ferrimagnetic (PM–FIM) transition at Curie temperature $T_C=57$ K and the first-order structural phase transition (T_S) around 53 K, which coincides with the long range OO of t_{2g} orbits in V-3*d* electrons. The cubic-to-tetragonal transformation can be achieved by using a magnetic field which accompanies a large change of lattice striction. This means that a field-induced switching of crystal structure takes place, indicating strong coupling between the degrees of spin and orbital freedom. Controlling the lattice degree of freedom by adjusting the applied magnetic field, there are some fascinating material functionalities in MnV_2O_4, such as giant magnetic field-induced strain [3] and the magnetocaloric effect [11,12]. Despite the significant interest in materials from the viewpoint of both physics and engineering, the nature of the PM–FIM transition of MnV_2O_4 is still not clear. On the other hand, from our former work, we find that the substitution of V ions by Al ones can obviously affect the magnetic interaction in MnV_2O_4; for example, the long range OO disappears. Therefore, to understanding in detail the nature of PM–PIM transition of spinel vanadates is needed. As we know, the critical exponents usually provide some useful extra information about the nature of the magnetic phase transition. From the reported results, the critical behavior of MnV_2O_4 might belong to the 3D Heisenberg or 3D Ising model [8,10,13]. In order to understand the possible reasons of the disappearance of OO and the nature of PM–FIM transition in Al-doped MnV_2O_4, in this paper, we study the critical behavior of $MnV_{1.95}Al_{0.05}O_4$ and compare it with that of MnV_2O_4. We find that the critical behavior of $MnV_{1.95}Al_{0.05}O_4$ belongs to the mean-field model and the collective interaction between V ions might have an important role in the OO of MnV_2O_4.

2. Experimental details

Polycrystalline samples of $MnV_{1.95}Al_{0.05}O_4$ were prepared by solid state reaction. The details of the sample preparations and their characterizations by x-ray diffraction and magnetization measurements have been reported in Ref. [14]. The magnetization measurements were performed with a quantum design superconducting quantum interference device magnetic property measurement system ($1.9\ \text{K}\le T\le 400\ \text{K}$, $0\ \text{T}\le H\le 5\ \text{T}$). The measured samples were machined into cylinders 6 mm length and 1 mm diameter, and the applied field was parallel to the longest semiaxis of the samples. So the field could exist throughout the

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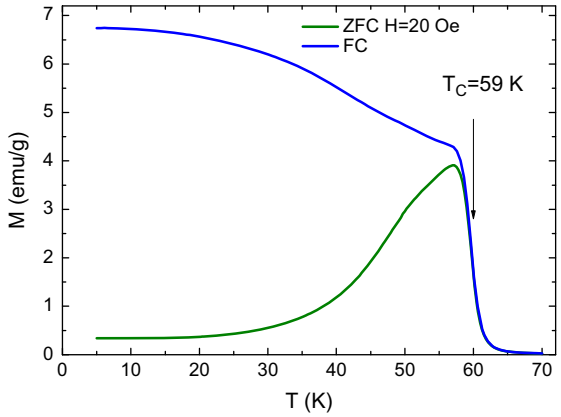

Fig. 1. Temperature dependence of magnetization measured in the ZFC and FC modes under applied magnetic field $H=20$ Oe. The T_C obtained from the maximum of dM/dT corresponds to the magnetic ordering temperature.

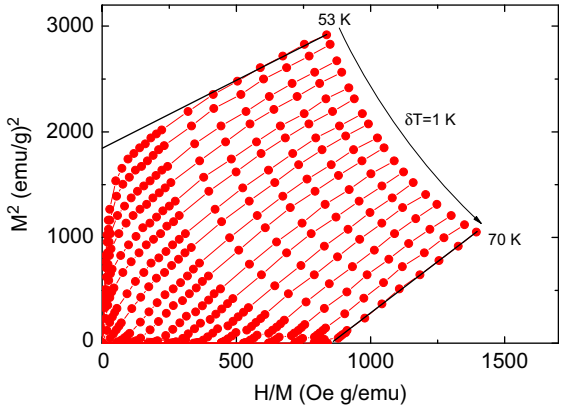

Fig. 2. M^2 *vs.* H/M plots for representative temperatures around the T_C.

samples and the sharp demagnetizing fields could be reduced as much as possible.

3. Results and discussion

Fig. 1 shows the temperature dependence of the magnetization $M(T)$ under the zero-field cooling (ZFC) and field cooling (FC) modes at an applied field of 20 Oe. The Curie temperature T_C (defined as the one corresponding to the peak of dM/dT in the curve of $M(T)$) is about 59 K, which is a little higher than that of MnV_2O_4. More detailed discussion can be found in the reported paper [14].

According to the scaling hypothesis, the second-order magnetic phase transition near the Curie point is characterized by a set of critical exponents, α, β, γ, δ, etc., and a magnetic equation of state [13]. The exponent α can be obtained from specific heat and β and γ from spontaneous magnetization and initial susceptibility, below and above T_C, respectively, while δ is the critical isotherm exponent. These exponents from magnetization measurements are given below:

$$M_S(T) = M_0|\varepsilon|^{-\beta}, \quad \varepsilon<0, \quad T<T_C \tag{1}$$

$$\chi_0^{-1}(T) = (h_0/M_0)\varepsilon^{\gamma}, \quad \varepsilon>0, \quad T>T_C \tag{2}$$

$$M = AH^{1/\delta}, \quad \varepsilon=0, \quad T=T_C \tag{3}$$

where $\varepsilon=(T-T_C)/T_C$ is the reduced temperature; M_0, h_0/M_0 and A are the critical amplitudes.

The magnetic equation of state in the critical region is written as

$$M(H,\varepsilon) = \varepsilon^{\beta} f_{\pm}(H/\varepsilon^{\beta+\gamma}), \tag{4}$$

where f_+ for $T>T_C$ and f_- for $T<T_C$ are regular functions. Eq. (4) implies that the $M|\varepsilon|^{-\beta}$ 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.

Fig. 2 shows a plot of M^2 *vs.* H/M around T_C with positive slopes indicating a second-order phase transition [15,16]. According to the mean-field theory near T_C, M^2 *vs.* H/M at various temperatures should show a series of parallel lines, and the line at $T=T_C$ has to pass through the origin. From the Arrott plots in Fig. 2, the curves below and above T_C can be extended smoothly into the H/M axis to yield the reliable values of $M_S(T,0)$ and $1/\chi_0(T)$, as the black lines are shown in Fig. 2.

$M_S(T,0)$ *vs.* T and $1/\chi_0(T)$ *vs.* T are plotted in Fig. 3(a). According to Eqs. (1) and (2), the critical exponents were determined to be $\beta=0.483(2)$ with $T_C=61.17(3)$ K from $M_S(T,0)$ *vs.* T and $\gamma=0.971(3)$ and $T_C=61.26(4)$ K from $1/\chi_0(T)$ *vs.* T. In addition, the critical exponents were also obtained by the Kouvel–Fisher (K–F) method [17]:

$$M_S(T)[dM_S(T)/dT]^{-1} = (T-T_C)/\beta, \tag{5}$$

$$\chi_0^{-1}(T)[d\chi_0^{-1}(T)/dT]^{-1} = (T-T_C)/\gamma. \tag{6}$$

According to these equations, plots of $M_S(T)[dM_S(T)/dT]^{-1}$ *vs.* T and $\chi_0^{-1}(T)[d\chi_0^{-1}(T)/dT]^{-1}$ *vs.* T should yield straight lines with slopes $1/\beta$ and $1/\gamma$, respectively, and the intercepts on the T axes equal T_C. Fig. 3(b) shows that the lines from the K–F method are linear approximately, which might suggest that the errors of the measurements can be nearly ignored and the derived values of $M_S(T,0)$ and $1/\chi_0(T)$ are reliable. We obtain the critical exponents $\beta=0.492(3)$ with $T_C=61.20(2)$ K and $\gamma=0.969(1)$ with $T_C=61.26(1)$ K. In Fig. 3(c), the critical isotherms M *vs.* H are plotted on log–log scale at the critical temperature 61.5 K, which is close to the T_C. According to Eq. (3), this should be a straight line in the high-field region with the slope $1/\delta$. The value of δ is about 2.951(4). The critical exponents from this static scaling analysis are related to the Widom scaling relation [18]

$$\delta = 1+\gamma/\beta. \tag{7}$$

From the above scaling relation Eq. (7) and the estimated values of β and γ from the K–F method, we obtain $\delta=2.970(5)$. The result obtained from the scaling relation is close to the estimated $\delta=2.951(4)$ value from the critical isotherm near the critical temperature. Thus, the critical exponents found in the K–F method obey the Widom scaling relation. The critical exponents obtained by the magnetization data are reliable and consistent with the scaling hypothesis.

In order to check whether our data in the critical region obey the magnetic equation of state as described by Eq. (4), $M|\varepsilon|^{-\beta}$ as a function of $H|\varepsilon|^{-\beta+\gamma}$ is plotted in Fig. 4 using the values of critical exponents obtained from the K–F method and $T_C\sim61.5$ K. The inset shows the same results on a log–log scale. All the points fall on 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 are reasonable.

The critical exponents can be also confirmed by the magnetic entropy change ΔS_M, which can be approximated as [19]

$$|\Delta S_M| = \sum \frac{M_i - M_{i+1}}{T_{i+1}-T_i}\Delta H \tag{8}$$

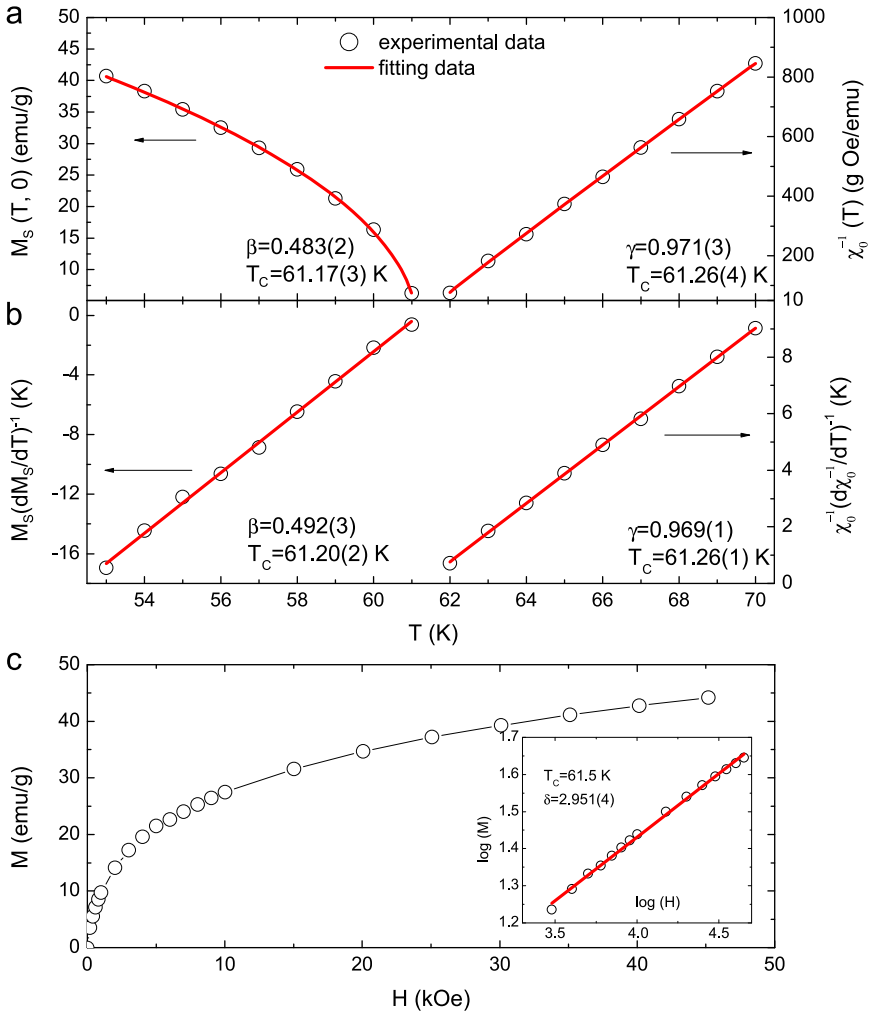

Fig. 3. (a) Temperature dependence of the spontaneous magnetization $M_S(T,0)$ and the inverse initial susceptibility $1/\chi_0(T)$ along with the fitting curves based on the power laws. (b) Kouvel–Fisher plots for the spontaneous magnetization and the inverse initial susceptibility. (c) Critical isotherms on a log–log scale for $MnV_{1.95}Al_{0.05}O_4$ at T_C. The inset shows ln M plotted as a function of ln H.

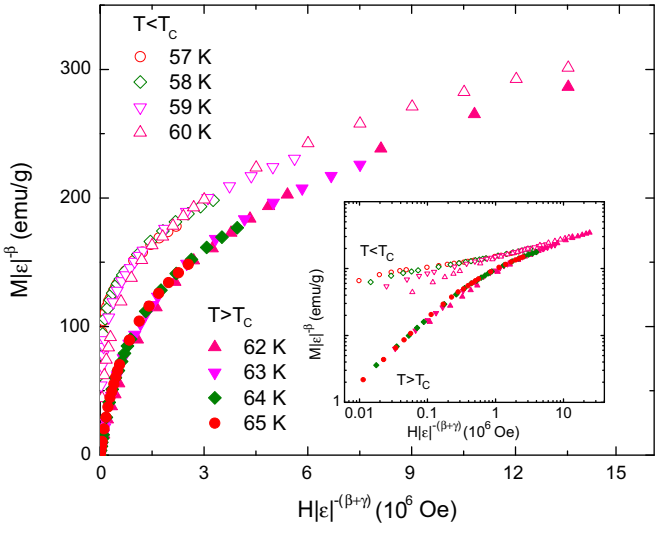

Fig. 4. Scaling plots for $MnV_{1.95}Al_{0.05}O_4$ below and above T_C using β and γ determined by the K–F method. The inset shows the same plot on log–log scale.

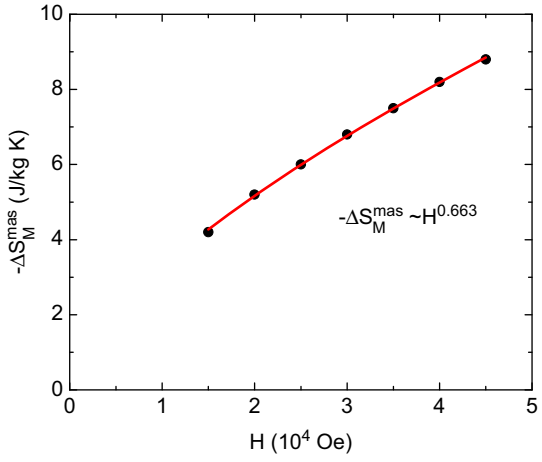

Fig. 5. H dependence of ΔS_M^{mas}(the solid curve is fitted).

A phenomenological universal curve for the field dependence of ΔS_M has been proposed as [20–22]

$$\Delta S_M|_{T=T_C} \propto H^n, \tag{9}$$

where $n=1+(\beta-1)/(\beta+\gamma)$. The ΔS_M around T_C is obtained according to Eq. (8). The ΔS_M for different magnetic fields can be found in Ref. [14]. Fig. 5 shows the H dependence of ΔS_M. From Eq. (9), we can get $n=0.666$. On the other hand, through the critical exponents obtained from the K–F method, the value of n is about 0.642, close to the value obtained from magnetic entropy,

Table 1
Comparison of critical parameters of $MnV_{1.95}Al_{0.05}O_4$ with the parent compound MnV_2O_4 reported in literatures and there of different theoretical models.

Material	Technique	β	γ	δ	Ref.
$MnV_{1.95}Al_{0.05}O_4$	Modified Arrott plot	0.483(2)	0.971(1)	3.010(5)	This work
	Kouvel–Fisher method	0.492(3)	0.969(1)	2.970(3)	This work
	Critical isotherm			2.951(4)	This work
MnV_2O_4	ac susceptibility	0.36(1)	0.59(3)	4.47(5)	10
MnV_2O_4	Neutron inelastic scattering	0.34(2)			8
Mean field model	Theory	0.5	1.0	3.0	13
3D Heisenberg model	Theory	0.365	1.386	4.80	13
3D Ising model	Theory	0.325	1.241	4.82	13

which further confirms that the obtained critical exponents are reliable.

The values of the critical exponents of $MnV_{1.95}Al_{0.05}O_4$ (present work), the theoretical values based on various models, and the critical values of the parent compound MnV_2O_4 obtained from different methods are listed in Table 1. Obviously, the critical exponents of $MnV_{1.95}Al_{0.05}O_4$ obtained from the magnetic data are close to the values of the mean-field model. The following information is also obtained from Table 1: the critical exponents are governed by the lattice dimension ($D=3$, in the present case), dimension of order parameter ($n=3$, magnetization) and range of interaction (short-range, long-range, or infinite) [23]. In homogeneous magnets the universality class of the magnetic phase transition is related to the range of the exchange interaction $J(r)=1/r^{d+\sigma}$, where d is the dimension of the system and σ is the range of interaction [23]. It has been argued that if σ is greater than 2, the 3D Heisenberg exponents ($\beta=0.365$, $\gamma=1.336$, $\delta=4.8$) are valid. The mean-field exponents ($\beta=0.5$, $\gamma=1$, $\delta=3$) are valid for σ less than 3/2. For the intermediate range $3/2<\sigma<2$, the exponents belong to different universality classes which depend on σ. For the case of MnV_2O_4, due to the complex phase transition near T_C, it is difficult to obtain the critical exponents from our present method. However, we can estimate the critical behavior of MnV_2O_4 from the reported ac susceptibility data, where the β value is close to that of a 3D Heisenberg ferromagnet [10], and the γ and δ values do not belong to any model. From the data of neutron inelastic scattering, the β value is between those of the 3D Ising model and 3D Heisenberg one [8]. This difference might be due to the data obtained from different methods. Although we cannot decide the critical behavior of MnV_2O_4, we can see that the critical behavior of $MnV_{1.95}Al_{0.05}O_4$ is much different from that of MnV_2O_4. And we can conclude that the substitution of V ions by Al ones obviously affects the critical behavior of $MnV_{1.95}Al_{0.05}O_4$.

As is well known, the ferromagnetism of MnV_2O_4 is affected by the strong coupling between spin, lattice and orbital degrees of freedom. Furthermore, the V^{3+} ions occupy the vertices of a tetrahedron and their mutual antiferromagnetic superexchange interactions are topologically frustrated. The directions of Mn ions and V ones are not parallel. The ground state of MnV_2O_4 is non-collinear FIM. From the critical exponents obtained from neutron inelastic scattering and ac susceptibility experiments, MnV_2O_4 might be a 3D magnet with short-range interactions, and the γ values obtained from different methods are close to that of the 3D Ising model or 3D Heisenberg one. From the results of $MnV_{1.95}Al_{0.05}O_4$, the critical behavior belongs to the long range interaction mean-field model. The possible reason is that the superexchange of V ions is collective. Due to the strong coupling between the lattice, spin and orbital degrees of freedom in system, the collective interaction between the V ions disappears or becomes much weaker for Al-ion doped sample than for the parent compound, so the magnetic direction of V ions tends to disorder or becomes parallel to that of Mn ones. On the other hand, the frustration interaction between the V ions becomes weak and the long range ferromagnetic interaction of $MnV_{1.95}Al_{0.05}O_4$ increases. So the critical behavior is close to that of the long range mean-field model and the critical temperature 61 K (obtained from K–F method) is a little larger than 56 K of MnV_2O_4. Due to the strong coupling between the spin, orbital and lattice degree of freedoms, the collective interaction between V ions has important role in the origin of OO in MnV_2O_4. For $MnV_{1.95}Al_{0.05}O_4$, the collective interaction between V ions is obviously destroyed due to the impurity of Al ions; therefore, the long range OO disappears. However, in order to clear the magnetic structure of $MnV_{1.95}Al_{0.05}O_4$, more experiments are needed. For the explicit universality class of $MnV_{1.95}Al_{0.05}O_4$, the high purity single crystal is also required for its critical research.

4. Conclusion

In summary, we investigate the critical properties of the spinel vanadate $MnV_{1.95}Al_{0.05}O_4$ by the Kouvel–Fisher method, and critical isotherm analysis. Reliable critical exponents $\beta=0.492$ (3), $\gamma=0.969(1)$ and $\delta=2.951(4)$ are obtained. The critical exponents are confirmed by the field dependence of the magnetic entropy change relation $\Delta S_M|_{T=T_C} \propto H^n$ with $n=1+(\beta+1)/(\beta+\gamma)$. The critical behavior of $MnV_{1.95}Al_{0.05}O_4$ agrees with the prediction of the mean-field model with long range interaction. Compared with MnV_2O_4, the different critical behavior of $MnV_{1.95}Al_{0.05}O_4$ might be because the doped Al ions destroy the collective frustration interaction between V ions. The ferromagnetism of $MnV_{1.95}Al_{0.05}O_4$ is mainly related to the long range ferromagnetic interaction of Mn ions.

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