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Critical behavior of multiferroic hexagonal $R\mathrm{MnO_3}$

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Using a microscopic model and a Green's function technique we have studied the critical behavior of some multiferroics such as hexagonal $R\mathrm{MnO_3}$. The temperature dependence and the external field dependence of the magnetization and susceptibility are determined. The critical exponents β and γ are calculated. Applying the scaling laws α, δ, and ν are also obtained. The critical exponents are in very good agreement with the existing experimental data.

1 Introduction Magnetoelectric multiferroics, which show both magnetic and ferroelectric properties simultaneously, have been extensively investigated recently [1]. Around the phase transition temperatures in multiferroic substances are observed different anomalies in many experimental data. Despite extensive studies on bulk and nanostructured $\mathrm{BiFeO_3}$ (BFO) and hexagonal $R\mathrm{MnO_3}$ multiferroics there are not so many investigations of the critical behavior, of the critical exponents of multiferroic materials. Twenty years ago Ishibashi and Hidaka [2] have showed that systems with isosymmetric phase transitions at $T_C = 1200$ K, such as BFO, exhibit a phase diagram with tricritical points and critical end points and have the unusual mean-field critical exponents $\alpha = 2/3$, $\beta = 1/3$, and $\gamma = 2/3$ at the end points. Scott et al. [3] have extended that to show the critical exponents for the isosymmetric phase transitions in BFO $\delta = 3$, $\nu = 1/3$, and $\eta = 0$. Singh et al. [4] have found that fluctuations along the uniaxial direction in BFO diverge and exhibit critical slowing down (spectral narrowing) approaching T_C, with critical exponents $\nu = 0.63$ and γ (susceptibility) $= 1.24$ for the longitudinal fluctuations and $\nu = 0.63$ and $\gamma = 1.47$ for the transverse fluctuations. The exponent characterizing the magnetization as a function of temperature β is known to be $\approx$0.43 from birefringence [5] and 0.37 from Mossbauer hyperfine splittings [6].

Poirier et al. [7] have reported an ultrasonic investigation of the elastic moduli in hexagonal $\mathrm{YMnO_3}$. Strong anomalies in the elastic moduli below T_N are observed and described within the Landau free energy model. The critical exponent associated to the order parameter is calculated to $\beta = 0.42$ which is neither consistent with chiral XY (0.25) and chiral Heisenberg (0.30) universality classes or with XY (0.35) and Heisenberg (0.36) ones, but more in agreement with a conventional AFM long range order [8]. For $\mathrm{LaMnO_3}$ Alves et al. [9] have observed a similar value of $\beta = 0.42$, which is remarkably close to the exponent of free percolation on a 3D cubic lattice (0.41). From heat capacity measurements Tachibana et al. [10] have observed for the critical exponent $\alpha = -0.16$, whereas Katsufuji et al. [11] have obtained $\alpha = 0.25$ from dielectric susceptibility measurements. For ν Fabreges et al. [12] reported the value of 0.65.

2 The model The aim of the present paper is to calculate on the basis of a microscopic model the critical exponents β and γ for M and χ^{zz} of hexagonal multiferroic $R\mathrm{MnO_3}$ compounds. The Hamiltonian for multiferroic BFO and hexagonal $\mathrm{RMnO_3}$ with $T_C \gg T_N$ can be presented as [13]:

$$H = H^e + H^m + H^{me}. \tag{1}$$

H^e denotes the Hamiltonian for the ferroelectric subsystem within the framework of the transverse Ising model:

$$H^e = -\Omega \sum_i S_i^x - \frac{1}{2}\sum_{ij} J_{ij} S_i^z S_j^z, \tag{2}$$

where S_i^x, S_i^z are the spin-1/2 operators of the pseudo-spins, J_{ij} denotes the nearest-neighbor pseudo-spin interaction, Ω is the tunneling frequency. The mean polarization is

proportional to the z component of the pseudo-spins introduced in the transverse Ising model. In the ordered phase we have the mean values $\langle S^{\mathrm{x}}\rangle \neq 0$ and $\langle S^{\mathrm{z}}\rangle \neq 0$, and it is appropriate to choose a new coordinate system rotating the original one used in Equation (2) by the angle θ in the xz plane. The rotation angle θ is determined by the requirement $\langle S^{\mathrm{x}'}\rangle = 0$ in the new coordinate system.

H^m is the Hamiltonian for the magnetic subsystem, which is given by the Heisenberg Hamiltonian:

$$\begin{aligned} H^{\mathrm{m}} = &-\frac{1}{2}\sum_{<ij>} A_1(i,j)\mathbf{B}_i\cdot\mathbf{B}_j \\ &-\frac{1}{2}\sum_{[ij]} A_2(i,j)\mathbf{B}_i\cdot\mathbf{B}_j\,, \\ &-g\mu_{\mathrm{B}}H\sum_i B_i^z, \end{aligned} \tag{3}$$

where $\mathbf{B}_i$ is the Heisenberg spin operator at the site i, and the exchange integrals A_1 and A_2 represent the coupling between the nearest and next-nearest neighbors, respectively. $<ij>$ and $[ij]$ denote the summation over the nearest neighbors and the next nearest neighbors, respectively. H is an external magnetic field.

The coupling term is taken to be biquadratic:

$$H^{\mathrm{me}} = -g\sum_{<ij>}\sum_{kl} S_k^z S_l^z \mathbf{B}_i\cdot\mathbf{B}_j. \tag{4}$$

Here g is the coupling constant between the magnetic and the ferroelectric order parameters.

3 Green's function and critical exponents The retarded Green's function to be calculated is defined by:

$$G_{ij}(t) = \left\langle\left\langle B_i^+(t);\ B_j^-(0)\right\rangle\right\rangle. \tag{5}$$

For the approximate calculation of the Green's function we use a method proposed by Tserkovnikov [14]. After a formal integration of the equation of motion, one obtains

$$G_{ij}(t) = -i\theta(t)\left\langle\left[B_i; B_j^+\right]\right\rangle \exp\left(-iE_{ij}(t)t\right), \tag{6}$$

where

$$\begin{aligned} E_{ij}(t) = E_{ij} - \frac{i}{t}\int_0^t \mathrm{d}t' t' \Bigg(&\frac{\left\langle\left[j_i(t); j_j^+(t')\right]\right\rangle}{\left\langle\left[B_i(t); B_j^+(t')\right]\right\rangle} \\ &- \frac{\left\langle\left[j_i(t); B_j^+(t')\right]\right\rangle\left\langle\left[B_i(t); j_j^+(t')\right]\right\rangle}{\left\langle\left[B_i(t); B_j^+(t')\right]\right\rangle^2}\Bigg), \end{aligned} \tag{7}$$

with the notation $j_i(t) = [B_i,\ H_{\mathrm{interaction}}]$. The time-independent term

$$E_{ij} = \frac{\left\langle\left[[B_i,\ H]; B_j^+\right]\right\rangle}{\left\langle\left[B_i;\ B_j^+\right]\right\rangle} \tag{8}$$

is the energy in the generalized Hartree–Fock approximation (GHFA), called so by the author [14] probably because it includes all correlation functions and so goes beyond the Hartree–Fock approximation. The time-dependent term in Equation (7) includes damping effects.

The relative magnetization M for arbitrary spin value S in the direction of the magnetic field is equal to:

$$\begin{aligned} M = \langle B^z\rangle = \frac{1}{N}\sum_k \Bigg[&(S+0.5)\coth\left[(S+0.5)\frac{E_{\mathrm{m}}(\mathbf{k})}{k_{\mathrm{B}}T}\right] \\ &- 0.5\coth\left(0.5\frac{E_{\mathrm{m}}(\mathbf{k})}{k_{\mathrm{B}}T}\right)\Bigg]. \end{aligned} \tag{9}$$

E_{m} is the spin-wave energy in the generalized Hartree–Fock approximation:

$$\begin{aligned} E_{\mathrm{m}}(\mathbf{k}) = &\frac{1}{2\langle B^z\rangle}\frac{1}{N}\sum_q \left(A_1^{\mathrm{eff}}(\mathbf{q}) - A_1^{\mathrm{eff}}(\mathbf{k}-\mathbf{q})\right) \\ &\times\left(2\langle B_q^z B_{-q}^z\rangle - \langle B_{k-q}^- B_{k-q}^+\rangle\right) \\ &+\frac{1}{2\langle B^z\rangle}\frac{1}{N}\sum_q \left(A_2(\mathbf{q}) - A_2(\mathbf{k}-\mathbf{q})\right) \\ &\times\left(2\langle B_q^z B_{-q}^z\rangle - \langle B_{k-q}^- B_{k-q}^+\rangle\right) + g\mu_{\mathrm{B}}H \end{aligned} \tag{10}$$

with the renormalized exchange interaction constant A_1:

$$A_1^{\mathrm{eff}} = A_1 + 2gP^2\cos^2\theta. \tag{11}$$

The quantity $P(T) = 2\langle S^z\rangle$ is the relative polarization in the direction of the mean field. It is calculated in our previous paper [13] where we have investigated different static and dynamic electric and magnetic properties of multiferroic $R\mathrm{MnO_3}$ compounds.

The temperature dependence of $M(T) = \langle B^z\rangle$ was calculated numerically using parameters appropriate to the multiferroic $\mathrm{YMnO_3}$ [13]: $A_1 = 85\,\mathrm{K}$, $A_2 = -60\,\mathrm{K}$, $\Omega = 20\,\mathrm{K}$, $J = 3600\,\mathrm{K}$, $T_{\mathrm{N}} = 80\,\mathrm{K}$, $T_{\mathrm{C}} = 900\,\mathrm{K}$, $S = 2$ for the magnetic subsystem and $s = 0.5$ for the pseudospins. The exchange interaction constants are calculated from their relation to the critical temperatures, i.e., they are obtained from the expressions in the mean-field theory

$$A_1^{\mathrm{eff}} = 3k_{\mathrm{B}}T_{\mathrm{N}}/zS(S+1)$$

and

$$J^{\mathrm{eff}} = 3k_{\mathrm{B}}T_{\mathrm{C}}/zS(S+1),$$

where z is the number of nearest neighbors, S is the spin value, and k_{B} is the Boltzmann constant.

The critical exponent β describing the order parameter $\langle B^z \rangle$ is defined as [15]:

$$\langle B^z \rangle = A\left(\frac{T_C - T}{T_C}\right)^{\beta}, \quad \text{for} \quad T \to T_C^-. \tag{12}$$

β is independent of the magnitude of the spin, but dependent on the dimensionality of the lattice. It is calculated numerically for a three-dimensional lattice in the temperature range $5 \times 10^{-4} < |(T_C - T)/T_C| < 5 \times 10^{-3}$ from $\ln\langle B^z \rangle = \ln A + \beta \ln(1 - T/T_C)$. The following value is observed:

$$\beta = 0.421 \pm 0.006, \tag{13}$$

which is in very good agreement with the experimental data of Poirier et al. [7] for $YMnO_3$ ($\beta = 0.42$) and of Alves et al. [9] for $LaMnO_3$ ($\beta = 0.42$). It is close to the critical exponent theoretically predicted for the three-dimensional Heisenberg model. Chatterji et al. [16] have determined the spin wave dispersions in $YMnO_3$ by inelastic neutron scattering and obtained the temperature variation of the integrated intensity of the (100) reflection near to T_N ($T > T_N$) as: $I = I_n + I_0((T_N - T)/T_N)^{2\beta}$ with $\beta = 0.295 \pm 0.008$. The obtained value of β is close to that expected for a 3D XY or Ising system [17]. It must be noted, that β determined by this investigation cannot really be identified with the critical exponent. In order to determine the critical exponent β one should not refine T_N from the temperature dependence of the intensity of the magnetic Bragg peak but should be independently determined from the divergence of the diffuse intensity at the ordering temperature [17, 18]. Also a possible temperature variation of the extinction parameters may hinder the determination of the critical exponent [18]. Chatterji et al. [16] have not attempted such rigorous investigation of the critical exponent β. The exponent β of $YMnO_3$ determined by Roessli et al. [19] is $\beta = 0.187 \pm 0.002$ and is much lower than the value obtained in [16]. However, Roessli et al. [19] have fitted the intensity data belonging to non-critical range of temperatures and hence cannot be identified with the critical exponent. Gibbs et al. [20] reported a high-resolution powder neutron diffraction investigation of the structural behavior of the multiferroic hexagonal $YMnO_3$ between room temperature and 1403 K. They observed a transition at 1258 ± 14 K driven primarily by the antiferrodistortive K_3 mode. A weighted power-law fit of the form $K_3 = A(T_C - T)^{\beta}$ was performed on the K_3 data as a function of temperature in the range 913–1243 K. The critical exponent obtained is $\beta = 0.271 \pm 0.003$ with $T_C = 1271.5 \pm 0.1$ K and $A = 0.135 \pm 0.002$. But surprisingly, the authors [20] obtained an increasing of the polarization with raising temperature what is opposite to the results of other authors [13, 21]. It must be mentioned that Kim et al. [21] have done also distortion-mode analysis of synchrotron X-ray data in the range from 300 to 1000 K of $YMnO_3$. They obtained the behavior of the K_3 modes and a phase transition at $T_C \approx 920$ K.

We have observed the critical exponent γ from the longitudinal susceptibility χ^{zz} which is determined in the ordered phase by the relation $\mathrm{d}\langle B^z \rangle / \mathrm{d}H|_{H=0}$. It is calculated numerically in the same temperature range as for $\langle B^z \rangle$ to

$$\gamma = 1.280 \pm 0.012. \tag{14}$$

Unfortunately, we don not know experimental data about this critical exponent in multiferroic $RMnO_3$ materials. The critical exponent γ for a 3D Heisenberg model is calculated from field theoretical estimates to $\gamma = 1.386(4)$ (resummed perturbation series [22]) and to $\gamma = 1.390(10)$ (resummed ε-expansion [23]).

Applying the scaling laws [15] we can obtain also other critical exponents, for example α, δ, and ν:

$$\alpha = 2 - 2\beta - \gamma = -0.122, \tag{15}$$

$$\delta = (\gamma + \beta)/\beta = 3.945, \tag{16}$$

$$\nu = (2 - \alpha)/d = 0.707. \tag{17}$$

Tachibana et al. [10] reported from heat capacity measurements in $YMnO_3$ $\alpha = -0.16$, whereas Gamzatov et al. [24] obtained for $LaMnO_3$ $\alpha = -0.127$ which is close to the estimated exponent $\alpha = -0.120$ theoretically predicted for the three-dimensional Heisenberg model, rather than a XY model ($\alpha = -0.01$) or a chiral university class [chiral XY model – $\alpha = 0.34(6)$ and chiral Heisenberg model – $\alpha = 0.24(8)$] [5]. Our results confirm this statement.

Fabreges et al. [12] have calculated the temperature dependence of the correlation length and fit the critical exponent ν to 0.65(8). Singh et al. [4] data from Raman spectra in BFO are compatible (in respect of both peak intensity divergence and linewidth narrowing) with the original study of spin fluctuations in uniaxial antiferromagnets by Schulhof et al. [25]. They found that fluctuations along the uniaxial direction diverge and exhibit critical slowing down (spectral narrowing) approaching T_C, with critical exponents $\nu = 0.63$ and γ (susceptibility) $= 1.24$ for the longitudinal fluctuations and $\nu = 0.63$ and $\gamma = 1.47$ for the transverse fluctuations. The correlation length exponent is $\nu = 0.64$–0.70 for 3D-Ising or Heisenberg models [26]. Holm and Janke [27] reported for the 3D Heisenberg model using a single-cluster Monte Carlo study $\nu = 0.704 \pm 0.006$. For comparison, the field theoretical estimates are $\nu = 0.705(3)$ (resummed perturbation series [22]), $\nu = 0.710(7)$ (resummed ε-expansion [23]). Recently, Griffin et al. [28] have studied the scaling behavior in the hexagonal multiferroic $RMnO_3$, R = Sc, Y, Dy–Lu, which are proposed as a model system for testing the Kibble–Zurek mechanism, and observed $\nu = 0.6717$.

4 Conclusions Basing on Eqs. (13)–(17) it may be concluded that the proposed model for investigation of the static and dynamic properties of the hexagonal multiferroics $RMnO_3$ [13] describes also very well the critical behavior of

these substances and that the method and the approximation applied here give values for the critical exponents, which are in very good agreement with the experimental data for $R\mathrm{MnO_3}$ compounds. Finally, the critical behavior of the multiferroic hexagonal manganites $R\mathrm{MnO_3}$ is close to a 3D-Heisenberg universality class, rather than to a XY model or a chiral university class (chiral XY model and chiral Heisenberg model).

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References

[1] K. F. Wang, J.-M. Liu, and Z. F. Ren, Adv. Phys. **58**, 321 (2009).
[2] Y. Ishibashi and Y. Hidaka, J. Phys. Soc. Jpn. **60**, 1634 (1991).
[3] J. F. Scott, M. K. Singh, and R. S. Katiyar, J. Phys.: Condens. Matter **23**, 022202 (2011).
[4] M. K. Singh, W. Prellier, M. P. Singh, R. S. Katiyar, and J. F. Scott, Phys. Rev. B **77**, 144403 (2008).
[5] J.-P. Rivera and H. Schmid, Ferroelectrics **204**, 23 (1997).
[6] C. Blaauw and F. van der Woude, J. Phys. C, Solid State Phys. **6**, 1422 (1973).
[7] M. Poirier, F. Laliberte, L. Pinsard, and A. Revcolevschi, Phys. Rev. B **76**, 174426 (2007).
[8] M. F. Collins and O. A. Petrenko, Can. J. Phys. **75**, 605 (1997).
[9] E. Alves, T. Agne, J. S. Amaral, V. S. Amaral, J. P. Arajo, J. M. D. Coey, N. A. Babushkina, J. G. Correia, H.-U. Habermeier, A. L. Lopes, A. A. Loureno, J. G. Marques, T. M. Mendona, M. S. Reis, E. Rita, J. C. Scares, J. B. Sousa, R. Suryanarayanan, P. B. Tavares, Y. Tokura, Y. Tomioka, A. Vantomme, J. M. Vieira, and U. Wahl, CERN/INTC 2005 016, INTC-P132 Addl (2005).
[10] M. Tachibana, J. Yamazakiu, H. Kawaji, and T. Atake, Phys. Rev. B **72**, 064434 (2005).
[11] T. Katsufuji, S. Mori, M. Masaki, Y. Moritomo, N. Yamamoto, and H. Takagi, Phys. Rev. B **64**, 104419 (2001).
[12] X. Fabreges, I. Mirebeau, S. Petit, P. Bonville, and A. A. Belik, Phys. Rev. B **84**, 054455 (2011).
[13] J. M. Wesselinowa and St. Kovachev, J. Appl. Phys. **102**, 043911 (2007).
[14] Yu. Tserkovnikov, Theor. Math. Phys. **7**, 250 (1971).
[15] H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena (Clarendon Press, Oxford, 1971).
[16] T. Chatterji, Pramana **71**, 847 (2008).
T. Chatterji, S. Ghosh, A. Singh, L. P. Regnault, and M. Rheinstadter, Phys. Rev. B **76**, 144406 (2007).
[17] M. F. Collins, Magnetic critical scattering (Oxford University Press, Oxford, 1989).
[18] R. A. Cowley, in: Methods of Experimental Physics, Vol. 23, Part C, edited by K. Skold and D. L. Price (Academic Press, Inc., 1987).
[19] B. Roessli, S. N. Gvasaliya, E. Pomjakushina, and K. Conder, JETP Lett. **81**, 287 (2005).
[20] A. S. Gibbs, K. S. Knight, and P. Lightfoot, Phys. Rev. B **83**, 094111 (2011).
[21] J. Kim, Y. M. Koo, K.-S. Sohn, and N. Shin, Appl. Phys. Lett. **97**, 092902 (2010).
[22] J. C. Le Guillou and J. Zinn-Justin, Phys. Rev. B **21**, 3976 (1980).
[23] J. C. Le Guillou and J. Zinn-Justin, J. Physique Lett. **46**, L137 (1985).
[24] A. G. Gamzatov, Sh. B. Abdulvagidov, A. M. Aliev, K. Sh. Khizriev. A. B. Batdalov, O. V. Melnikov, O. Yu. Gorbenko, and A. R. Kaul, Phys. Solid State **49**, 1769 (2007).
[25] M. P. Schulhof, P. Heller, R. Nathans, and A. Linz, Phys. Rev. B **1**, 2304 (1970).
[26] M. A. Moore, D. Jasnow, and M. Wortis, Phys. Rev. Lett. **22**, 940 (1969).
[27] C. Holm and W. Janke, Phys. Rev. B **48**, 936 (1993).
[28] S. M. Griffin, M. Lilienblum, K. Delaney, Y. Kumagai, M. Fiebig, N. A. Spaldin, arXiv:1204.3785v1 (2012).

