Dilution-Controlled Quantum Criticality in Rare-Earth Nickelates

J.V. Alvarez,[1] H. Rieger,[2] and A. Zheludev[3]

[1]*Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, USA*
[2]*Theoretische Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany*
[3]*Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6393, USA*

(Received 21 December 2003; published 5 October 2004)

A microscopic model for the diluted spin-mixed compounds $(R_xY_{1-x})_2BaNiO_5$ (R = magnetic rare earth) is studied using quantum Monte Carlo simulations. The ordering temperature is shown to be a universal function of the impurity concentration x and the intrinsic Ni-chain correlation length. An effective model for the critical modes is derived. The possibility of a quantum critical point driven by the rare-earth concentration and the existence of a quantum Griffiths phase in the high dilution limit is investigated. Several possible experimental approaches to verify the results are put forward.

DOI: 10.1103/PhysRevLett.93.156401 PACS numbers: 71.10.Pm, 74.50.+r, 71.20.Tx

An increasing number of low-dimensional quantum magnets are being realized in materials artificially modified at nanometer scales. The use of layered structures, a dilution, and/or a combination of magnetic species with different magnetic moments establish complex geometries that enhance the role of quantum correlations. The resulting competing ground states, quantum critical points, and coexistence of classical and quantum features are of great current interest in condensed matter and interdisciplinary physics. The family of mixed-spin quantum antiferromagnets (AFs) $(R_xY_{1-x})_2BaNiO_5$ (R = magnetic rare earth) provides a unique experimental basis to discuss these issues. The $x = 0$ compound is an excellent realization of the one-dimensional (1D) $S = 1$ Heisenberg model, thanks to a linear-chain arrangement of the magnetic Ni^{2+} ions. Neutron scattering experiments [1] confirmed a spin liquid behavior and revealed a Haldane gap of about 10 meV in the magnetic excitation spectrum. Interchain interactions, negligible for $x = 0$, can be controlled by substituting the intercalated nonmagnetic Y^{3+} by magnetic rare earths. For $x = 1$ the system orders antiferromagnetically at $T_N = 10$–50 K, depending on R [2]. The spin dynamics is characterized by a coexistence and frequency separation of semiclassical (spin waves) and quantum (Haldane-gap modes) excitations [3–5]. By now, this phenomenon has been extensively studied experimentally [3], analytically [4,5], and numerically [6,7].

The focus of the present Letter, however, is the role of randomness and disorder for $0 < x < 1$. Previous studies were aimed at understanding the large-x limit. Because of a finite intrinsic correlation length in Haldane spin chains ($\xi_{ch} \approx 7$ lattice units), for $x \approx 1$ disorder is effectively averaged out. The problem is then merely a rescaled version of the $x = 1$ case [3,4]. For $x \lesssim 1/\xi_{ch}$ the mean distance between magnetic rare-earth centers becomes comparable to ξ. To date, very little is known of this regime, beyond the fact that it should represent qualitatively new physics. Below we develop a numerical approach to this interesting problem. Our calculations predict an unusual percolation mechanism for $(R_xY_{1-x})_2BaNiO_5$ and related systems. We show that the ordering temperature is a *universal* function of $x\xi_{ch}$ if $x \ll 1$. In addition, we derive an effective model for the critical modes, discussing whether the system is ordered down to zero concentration x or can support a quantum critical point.

Model.—A microscopic model for $(R_xY_{1-x})_2BaNiO_5$ was proposed in Refs. [4,7] and studied in detail for $x = 1$ [7]. The corresponding spin Hamiltonian includes a part that describes the individual Haldane spin chains and an additional interchain interaction term. The former contains no disorder and is independent of the doping level x. In contrast, the interaction term involves spin operators for the intercalated rare-earth ions and directly reflects the effect of dilution. In the present work we consider two variations of this model:

$$H_1 = H_{c-c} + J\sum_{ij} \mathbf{S}_{i,2j}\mathbf{S}_{i+1,2j}, \tag{1}$$

$$H_2 = H_{c-c} - J\sum_{ij} S^z_{i,2j}S^z_{i+1,2j} + \Gamma\sum_{ij} S^x_{i,2j}$$
$$\text{with } H_{c-c} = J_c\sum_{ij} \epsilon_{i,2j+1}s^z_{i,2j+1}(S^z_{i,2j} + S^z_{i,2j+2}), \tag{2}$$

where i and j label the spin in the directions parallel and perpendicular to the chains, respectively. Both Hamiltonians have a common interchain interaction term H_{c-c}. ϵ is a random variable representing the stochastic occupation of the interchain sites with moments $s_{i,2j+1}$ corresponding to the rare earths with probability density $\rho(\epsilon) = x\delta(\epsilon - 1) + (1 - x)\delta(\epsilon)$. As argued in Refs. [4,7], Kramers rare-earth ions in the $(R_xY_{1-x})_2BaNiO_5$ structure can be modeled by $S = 1/2$ pseudospins with anisotropic (Ising-type) R-Ni exchange interactions J_c.

The two Hamiltonians differ in their description of the gapped spin chains. In model (1) the chains are $S = 1$ Heisenberg systems, as in the real material. This model is thus well suited for calculations of realistic ordering

temperatures and direct comparisons with experimental data. However, model (2) allows more flexibility for a conceptual study of the problem. It incorporates quantum Ising spin chains in a transverse field (ITF) with $\Gamma > J$ (paramagnetic gapped regime) [8]. The ITF model is in the same universality class as $S = 1$ Haldane spin chains and shares with it many common features [9]. The ground state in both cases is a spin liquid with exponentially decaying correlations with the same asymptotic power-law corrections. The spectrum is gapped, and the low-lying excitations are long-lived magnonlike states with a dispersion minimum near the 1D AF zone center. Though the symmetries of ITF and Haldane spin chains are different [the full SU(2) symmetry of the Heisenberg model is reduced to Z_2 in the ITF], it matters little in our case. Indeed, in both *complete* Hamiltonians (1) and (2) SU(2) symmetry is *explicitly broken* by the Ising nature of J_c. The advantage of using the ITF model for our purpose is that it allows us to tune the intrinsic in-chain correlation length $\xi_{\rm ch}^{-1} = \log(\frac{\Gamma}{J})$ through the entire range between the free-spin limit $\xi_{\rm ch} = 0$ to chain criticality $\xi_{\rm ch} \to \infty$. This, in turn, enables a study of the fine interplay between the doping level x and the correlation length, and the resulting unique percolation behavior.

Using an efficient quantum Monte Carlo cluster algorithm [10,11], we first computed the critical temperature for a large range of transverse fields and concentrations in (2) using a periodic dilution pattern. In Fig. 1(a) we plot, for different concentrations, the critical temperature T_c as a function of $\xi_{\rm ch}$. The figure shows a crossover between regions I and II when the temperature is of the order of the gap of the independent chain $T = \Delta_{\rm ch} = 2(\Gamma - J)$ considered as a separate entity inside the whole system. The key to understand how the ordering temperatures depend on x in this system is the universal dependence of the critical temperature in the dimensionless variable $x\xi_{\rm ch}$, which is the ratio between the correlation length in the chain $\xi_{\rm ch}$ and the average distance between R ions x^{-1}. For moderate values of the transverse magnetic field, different concentration curves collapse when $x \ll 1$ [see Fig. 1(b)]. This suggests that the effective degrees of freedom that become critical interact with an effective coupling that decreases with the distance between the R magnetic moments and the correlation length in the chains. To clarify the nature of such degrees of freedom we computed the critical exponents using the conventional finite-size analysis of the order parameter (see Fig. 2). We found that the exponents are compatible with the *classical* 2D Ising model both for periodic and disordered dilution patterns (note that the critical behavior of the randomly diluted 2D Ising model differs from the one of the pure 2D Ising model only by logarithmic corrections [12]). This suggests that the building blocks of the effective critical model are classical Ising spins.

Effective 2D anisotropic Ising model.—To express these ideas in quantitative form we have derived a low-energy effective model for both Hamiltonians using a canonical transformation. The central idea underlying this effective model is that the local moments generated by the presence of the R ion between two chains are coupled due to the stiffness of the finite chains connecting them. We first study the spectrum of the local Hamiltonian of the Ni-R-Ni three-spin block: $h_j = J_c s^z_{i,j}(S^z_{i,j-1} + S^z_{i,j+1}) + \Gamma(S^x_{i,j-1} + S^x_{i,j+1})$. The z component of the central spin $s^z_{i,j}$ representing the magnetic moment in the R^{3+} ion is a good quantum number. That symmetry breaks the block spectrum in two orthogonal sectors. The ground state is twofold degenerated and each ground state belongs to distinct sectors. We label these states $|\Uparrow\rangle$ and $|\Downarrow\rangle$ that have opposite values for the expectation value of the *total* z component of block spin $M^z = \pm(s^z + \bar{S})$, where $\bar{S} = \mu(1 + \mu^2)^{-1/2}$ is the magnetization expectation value of the two outer spins and $\mu = J_c/2\Gamma$. There is always a finite gap $\Delta_B = [(J_c/4)^2 + \Gamma^2]^{1/2}$ to the first excited states above this doublet (level crossing of local states is forbidden by the symmetry). All the for-

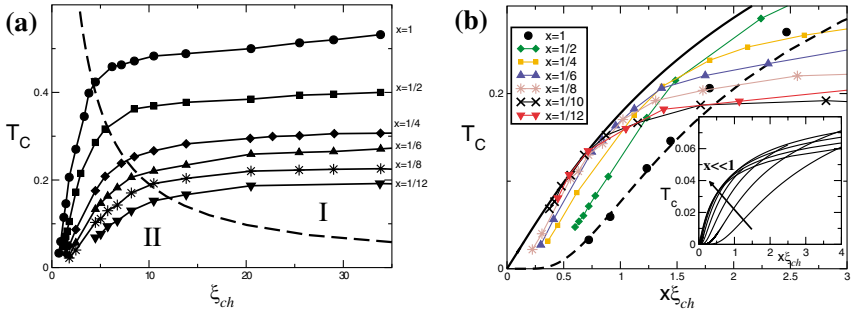

FIG. 1 (color online). (a) Critical temperature T_c as a function of the correlation length in the *independent* ITF chain $\xi_{\rm ch}$, for different concentrations of R using a periodic dilution pattern and $J_c = 0.2$. The dashed line indicates the value of the gap of the independent chain ($k_B = \hbar = 1$). This energy scale separates the two completely different behaviors at $T_c = \Delta_{\rm ch}$ showing that the 1D features of the gapped chains survive even at the critical point. (b) Universal dependence of the critical temperature on the dimensionless variable $x\xi_{\rm ch}$ at high dilutions. The dashed line is a fit to $T_c(x = 1)$ using 2D ANI with $J_\parallel = J\bar{S}^2$ and $J_\perp = \kappa J_c \bar{S}^2 (\kappa = 2.25)$. The thick solid line corresponds to the same model with $J_\parallel = \rho_0 \exp(-1/x\xi_{\rm ch})$ with $\rho_0 = 1.15J$ and $J_\parallel = 0.13J$. Inset: $T_c(x\xi_{\rm ch})$ for 2D ANI with $J_\parallel = \rho(x, \xi_{\rm ch})\bar{S}^2$, $J_\perp = \bar{S}^2$ with $\rho(x, \xi_{\rm ch})$ being the stiffness of the independent ITF chain.

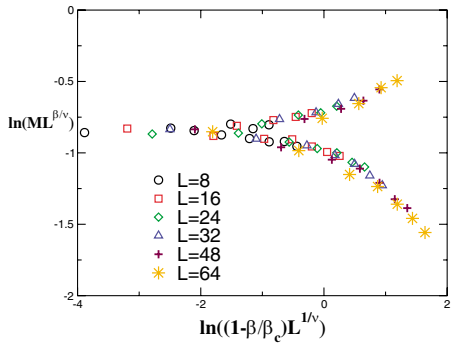

FIG. 2 (color online). Finite-size analysis of the order parameter in the vicinity of the critical point for $J_c = 0.1$, $\Gamma = 1.25$, $x = 0.5$, and $T_c = 0.13$ in the randomly diluted system. Here the data collapse is achieved with $\beta = \frac{1}{8}$ and $\nu = 1$, the exponents of the 2D Ising model.

mulas are valid also for the $S = 1$ system taking $J_c \to 2J_c$ and $\Gamma \to 0$. We consider now the dominant couplings in the low dilution limit: those between two effective local moments on neighboring sites along the direction of the chains $i, i+1$. For model (2) this coupling is exclusively of the Ising type (there is no spin-flip process along the chains). The leading contribution to this coupling is given by the energy necessary to create a domain wall between blocks i and $i+1$, $J_\parallel = \frac{1}{2}(\langle \Uparrow_i, \Downarrow_{i+1} | h^z_\parallel | \Uparrow_i, \Downarrow_{i+1}\rangle - \langle \Uparrow_{i+1}, \Uparrow_i | \times h^z_\parallel | \Uparrow_i, \Uparrow_{i+1}\rangle)$, where $h^z_\parallel = J(S^z_{i,j-1}S^z_{i+1,j-1} + S^z_{i,j+1}S^z_{i+1,j+1})$. Using the explicit form of the block eigenstates we can prove that the effective coupling is $J_\parallel = J\bar{S}^2 + O(J^2/\Delta_B)$, i.e., the product of the energy to create a domain wall in each chain times the expectation value of the magnetization in the two outer spins of the block. In the case of $S = 1$ Heisenberg chains we have off-diagonal terms $h^{xy}_\parallel = J/2(S^+_{i,j-1}S^-_{i+1,j-1} + S^+_{i,j+1}S^-_{i+1,j+1}) + \text{H.c.}$ However, the s^z_i are still good quantum numbers and this prevents spin flipping in the effective Hamiltonian. This is the strongest argument in favor of the low-energy equivalence of models (1) and (2). An essentially identical argument can be applied in the high dilution limit to compute effective coupling between two distant local magnetic moments obtaining now $J_\parallel = 2\bar{S}^2\rho$, where $\rho = E(s_j = s, s_k = -s) - E(s_j = s, s_k = s)$ and $E(s_j, s_k)$ is the energy of the chain connecting the two blocks with spin s_j in site j and s_k in site k. In other words, ρ is the energy difference between antiparallel and parallel spins at the end of the chain, and it is directly related to the static stiffness of the (finite) chain which is nonzero even in the paramagnetic case. In both chain models the asymptotic behavior is $\rho \sim \rho_0 \times \exp(-|k-j|/\xi_{\text{ch}})$. At $T_c \ll \Delta_B$ the thermal population of excited states above the doublet is strongly suppressed and the block can be described by an Ising variable. The emerging effective model is a 2D anisotropic Ising (2D ANI) model with T_c given by $\sinh\beta_c J_\parallel \sinh\beta_c J_\perp = 1$ and $T_c = 1/\beta_c$. In the inset of Fig. 1(b) we show $T_c(x\xi_{\text{ch}})$ taking the expression of ρ from an isolated ITF chain [8], which shows good qualitative agreement with the numerical at periodic dilutions. The effect of the quantum fluctuations in the microscopic model is integrated out in the effective classical model and can be formally separated into two parts: the reduction of the effective magnetic moment associated to the Ising spins $|\Uparrow\rangle, |\Downarrow\rangle$ and the exponential decay of the couplings in the direction parallel to the chains. The former dominates the behavior of T_c with $x = 1$ (dashed line). At $x \ll 1$ it is the exponential dependence of $J_\parallel$ which dominates the value of T_c (solid line).

We have also simulated random dilutions in regions I and II for model (2) and for model parameters relevant to $(Nd_xY_{1-x})_2BaNiO_5$ in model (1) [7] [see Fig. 3(a)]. For $\Gamma = 1.05$ and $J_c = 0.2$ (diamonds) the system is in region I $T_c > \Delta_{\text{ch}}$ showing a sublinear dependence on x $T_c(x) = 0.52x^{0.439}$. On the other hand, for $\Gamma = 1.75$ and $J_c = 0.1$ (squares) the system is well inside region II $T_c > \Delta_{\text{ch}}$. A linear fit gives $T_c(x) = 0.069x - 0.004$ (the constant is much smaller than the error determining T_c). The $S = 1$ system with $J_c = 0.35J$ (triangles) lies also in region II (triangles) and shows an interesting change of behavior at $x \sim \xi^{-1}_{\text{ch}}$ that may be compatible with the $T_c \sim x\xi_{\text{ch}}$ described above. The system $\Gamma = 1.25$ and $J_c = 0.1$ is closer to the crossover $T_c \sim \Delta_{\text{ch}}$ region, and it is harder to establish if ξ_{ch} is playing any special role.

Dilution-driven QCP.—A system of gapped chains may require a finite value of the perpendicular coupling to establish order. This is especially clear when the perpendicular coupling is spin isotropic. Therefore it is important to study whether the existence of order at finite value of x is robust against the presence of spin-flip processes between the central spin in R and its Ni^{2+} neighbors, $h^{xy}_\perp = (J^{xy}_c/2)s^+_{i,j}(S^-_{i,j-1} + S^-_{i,j+1}) + \text{H.c.}$ A small value for J^{xy}_c breaks the conservation law for s^z_i and establishes quantum coherence between $|\Uparrow\rangle$ and $|\Downarrow\rangle$. In leading order, it has the same effect of a transverse magnetic field acting on the spin blocks. If $J^{xy}_c \ll \Delta_B$ we can compute within second order perturbation theory the matrix element $\Gamma_{\text{eff}} = \langle \Downarrow | h^{xy}_\perp | \Uparrow\rangle = (J^{xy}_c)^2/4\Delta_B$. This Γ_{eff} should not be confused with the original transverse field Γ in the chains. The effective model at $T = 0$ is now a 2D ITF which has a QCP for $\frac{\Gamma}{J} = 3.044(2)$ [13]. In the original model this translates into a QCP governed by the concentration, $x_c^{-1} = \xi_{\text{ch}} \log(\frac{\Gamma_{\text{eff}}}{\alpha\rho_0})$, where α is a numerical constant. In Fig. 3(b) we show the generic zero-temperature phase diagram that we expect for the randomly diluted system: Since the critical value for the effective matrix element Γ_{eff} vanishes exponentially for $x \to 0$, strongly diluted ($x \ll 1$) experimental systems are most probably in the paramagnetic phase. Nevertheless, since the system is disordered and close to a QCP at $\Gamma_{\text{eff}}(x)$, one expects the region $\Gamma_{\text{eff}} < \Gamma_c$ to be a quantum Griffiths-McCoy phase [14–16], in which various physical observables display a singular behavior and experimental measurements should show strong sample to

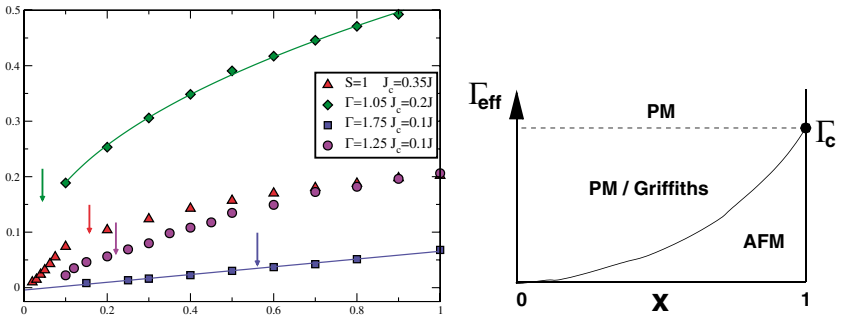

FIG. 3 (color online). (a) Critical temperature $T_c(x)$ as for Hamiltonians (1) and (2) with different model parameters. A randomly diluted pattern is used in all the cases. The arrows show the value of the inverse correlation length for each model. (b) Generic zero-temperature phase diagram of the randomly diluted system described in the text. The paramagnetic (PM) region is a Griffiths-McCoy region. Note that the phase boundary of the ordered phase approaches $\Gamma_{\text{eff}} = 0$ at $x = 0$ with an essential singularity. The value of Γ_c corresponds to the quantum critical point (QCP) of the pure system (see the text).

sample fluctuations as we actually observed in the numerical simulations. The usual phenomenological argument leading to, for instance, a diverging susceptibility in a diluted transverse Ising system close to but away from a QCP is the following [17,18]: Connected clusters with N spins appear with an exponentially small probability $p^N = \exp(-\lambda N)$ (p being the probability for an occupied site), but first order perturbation theory tells us that for small transverse field strengths the gap of this cluster is also exponentially small in the number of connected spins $\Delta \sim \exp(-\sigma N)$, leading to an exponentially large tunneling time. This implies, at zero temperature, a power-law behavior for the autocorrelation function $[\langle \sigma_i^z(t)\sigma_i^z(0)\rangle]_{\text{av}} \sim t^{-\lambda/\sigma}$, and thus an algebraic singularity of, for instance, the local zero-frequency susceptibility $\chi(\omega = 0) \sim T^{-1+\lambda/\sigma}$. These Griffiths-McCoy singularities are generic for a randomly diluted transverse Ising system (actually generic for any kind of disorder). In our case the dilution is such that no isolated finite clusters exist; nevertheless, parts of the system are more strongly coupled than others simply because there are more occupied interchain sites. Generic disorder, like random ferromagnetic bonds, also leads to Griffiths-McCoy singularities in nondiluted transverse Ising systems, as was demonstrated numerically [10]; hence we also expect them to be present in the system we are considering here.

Experimental implications.—Our central predictions, particularly the universal scaling of T_c, should be straightforward to verify on $(R_x Y_{1-x})_2 BaNiO_5$ powder samples by bulk magnetic and calorimetric measurements or by neutron diffraction. Conversely, the intrinsic chain correlation length can be effectively *measured* through measuring the x dependence of the ordering temperature. Those effects associated with strong disorder and algebraic singularities can be directly probed in more involved single-crystal neutron scattering experiments.

The work at ORNL was carried out under DOE Contract No. DE-AC05-00OR22725.

[1] J. Darriet and L. P. Regnault, Solid State Commun. **86**, 409 (1993); J. F. DiTusa *et al.*, Physica (Amsterdam) **194B–196B**, 181 (1994); T. Sakaguchi *et al.*, J. Phys. Soc. Jpn. **65**, 3025 (1996); G. Xu *et al.*, Phys. Rev. B **54**, R6827 (1998).
[2] E. García-Matres *et al.*, J. Solid State Chem. **103**, 322 (1993); J. Magn. Magn. Mater. **149**, 363 (1995).
[3] A. Zheludev *et al.*, Phys. Rev. Lett. **80**, 3630 (1998); T. Yokoo *et al.*, Phys. Rev. B **58**, 14 424 (1998); A. Zheludev *et al.*, Phys. Rev. B**61**, 11 601 (2000); J. Phys. Condens. Matter **13**, R525 (2001).
[4] S. Maslov and A. Zheludev, Phys. Rev. Lett. **80**, 5786 (1998).
[5] I. Bose and E. Chattopadhyay, Phys. Rev. B **60**, 12 138 (1999); E. Ercolessi *et al.*, Phys. Rev. B **62**, 14860 (2000).
[6] J. Lou, X. Dai, S. Quin, Z. Su, and L. Yu, Phys. Rev. B **60**, 52 (1999).
[7] J.V. Alvarez, R. Valenti, and A. Zheludev, Phys. Rev. B **65**, 184417 (2002).
[8] P. Pfeuty, Ann. Phys. (N.Y.) **57**, 79 (1970).
[9] G. Gomez-Santos, Phys. Rev. Lett. **63**, 790 (1989).
[10] C. Pich, A. P. Young, H. Rieger, and N. Kawashima, Phys. Rev. Lett. **81**, 5916 (1998).
[11] H. G. Evertz, G. Lana, and M. Marcu, Phys. Rev. Lett. **70**, 875 (1993).
[12] F. D. A. Aarao Reis, S. L. A. de Queiroz, and R. R. dos Santos, Phys. Rev. B **54**, R9616 (1996); Y. Tomita and Y. Okabe, Phys. Rev. E **64**, 036114 (2001); Vik. S. Dotsenko and V. I. Dotsenko, Zh. Eksp. Teor. Fiz. **33**, 40 (1981) [JETP Lett. **33**, 37 (1981)].
[13] H. Rieger and N. Kawashima, Eur. Phys. J. B **9**, 233 (1999).
[14] R. B. Griffiths, Phys. Rev. Lett. **23**, 17 (1969).
[15] B. M. McCoy, Phys. Rev. Lett. **23**, 383 (1969).
[16] H. Rieger and A. P. Young, *Quantum Spin Glasses*, Lecture Notes in Physics Vol. 492 (Springer-Verlag, Berlin, Heidelberg, New York, 1997).
[17] M. J. Thill and D. A. Huse, Physica (Amsterdam) **214A**, 321 (1995).
[18] H. Rieger and A. P. Young, Phys. Rev. B **54**, 3328 (1996); T. Ikegami, S. Miyashita, and H. Rieger, J. Phys. Soc. Jpn. **67**, 2761 (1998).