Symmetry analysis of the magnetic structures of bilayered manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ near $x=0.3$: Phase separations and percolation

Fan Zhong
*Department of Physics, University of Hong Kong, Hong Kong, People's Republic of China and Department of Physics, Zhongshan University, Guangzhou 510275, People's Republic of China**

Z. D. Wang
Department of Physics, University of Hong Kong, Hong Kong, People's Republic of China
(Received 3 May 2000)

We analyze the symmetry of the magnetic structures of tetragonal bilayered manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ with doping near $x=0.3$ and formulate a corresponding Landau theory of the phase transitions involved. It is shown that a phase with a single magnetic order cannot be canting though with a mixture of different magnetic orders can, as is possibly the case near $x=0.4$. Accordingly, a schematic magnetic phase diagram near $x=0.3$ is constructed which may consistently account for the controversial experimental observations. Possible phase separations and a percolation mechanism of the colossal magnetoresistance are discussed.

Recent extensive investigation of the so-called colossal magnetoresistance (CMR) Ref. 1 in doped perovskite manganites has stimulated considerable interest in relative bilayered compound $La_{2-2x}Sr_{1+2x}Mn_2O_7$ in an attempt to understand and to improve the sensitivity of the magnetoresistive response.[2–4] The material of interest is comprised of perovskite (La, Sr)MnO_3 bilayers separating by (La, Sr)O blocking layers, namely, the $n=2$ member of the Ruddlesden-Popper series of manganites (La, Sr)O$[$(La, Sr)$MnO_3]_n$. This quasi-two-dimensional nature promotes fluctuations that lower the critical temperature T_c of the magnetic transition and hence the relevant scale of a magnetic field for the huge magnetoresistance. As the tetragonal $I4/mmm$ symmetry of the material *a priori* lifts the degeneracy of the e_g orbitals of the Mn^{3+} ions, whose Jahn-Teller distortion was argued to be responsible for the CMR of the perovskite manganites[5], observation of antiferromagnetic (AFM) correlations above T_c of a paramagnetic (PM) to ferromagnetic (FM) transition in $La_{1.2}Sr_{1.8}Mn_2O_7$ was suggestive as an alternative origin to assist localization of carriers above T_c.[6] Importance of the AFM superexchange interaction shows up at the same doping level as canting of the ordered moments in neighboring layers within each bilayer as inferred from the sign reversal of the Mn-O bond compressibility below T_c.[7] Further neutron-scattering investigation of PM correlations provided evidence for the strong canting of the spins with an average angle that depends on both the magnetic field and the temperature above T_c owing to the weaker FM correlation within the bilayers.[8] The canting angle, in particular, changes from 86° at zero field to 74° at an external magnetic field of 1 T to 53° at 2 T at 125 K. Comprehensive neutron-diffraction studies, on the other hand, found that the canting angle increases from 6.3° at $x=0.4$ to 180° (A-type AFM) at $x=0.48$ at 10 K, while T_c decreases from 120 to 0 K, correspondingly. Moreover, the AFM correlations above T_c were identified as an intermediate phase whose order parameter decreases in an anomalous exponential manner upon increasing temperature to about 200 K.[9] Accordingly, the AFM correlations and more generally the magnetic structure seem to play an important role in the bilayered manganites.

Although the bilayered manganites exhibit an FM order below T_c with an easy axis at the layer for $0.32 \lesssim x \lesssim 0.4$, the magnetic structure at $x=0.3$ is somewhat complicated and so there exists no consensus. Perring *et al.*[10] proposed a bilayered AFM order of an intrabilayer FM and interbilayer AFM structure (denoted as AFM-B) with the easy axis along z below about 90 K from magnetic neutron diffraction. However, a substantial component within the layers rises up and then falls between 60 and 90 K or so. Argyriou *et al.*[11] by neutron diffractions and Heffner *et al.*[12] by muon spin rotation measurements reported, on the other hand, that their sample with the same doping involves two structurally similar phases: The major phase (hole poor) shows canting in a similar AFM-B structure with substantial components both in the plane and out of it. The minor phase (hole rich but $x<0.32$) differs from the major one only by its FM arrangement along z axis and its lower ordering temperature. However, as they pointed out, the assignment of the in-plane component is not so unambiguous. Also their in-plane AFM reflections become vanishingly small below about 60 K either. Still another scenario at the 30% doping is this: The magnetic structure changes from PM to AFM-B at about 100 K and then to FM at 70 K or so. The easy axis rotates correspondingly from in-plane in the AFM-B to z direction in the FM state.[4,13,14] From these experiments, whether there exists canting of spins at $x=0.3$ is still ambiguous. Noticing the importance of the magnetic correlations in the $x \gtrsim 0.4$ doping, clarification of the magnetic structure of the $x=0.3$ doping is a key to understand its characteristic transport behavior.[3,15]

In this paper, we show from symmetry analysis and a corresponding Landau theory that a single magnetic structure like AFM-B or FM order cannot be canting, though competition between them can. This result allows us to construct a

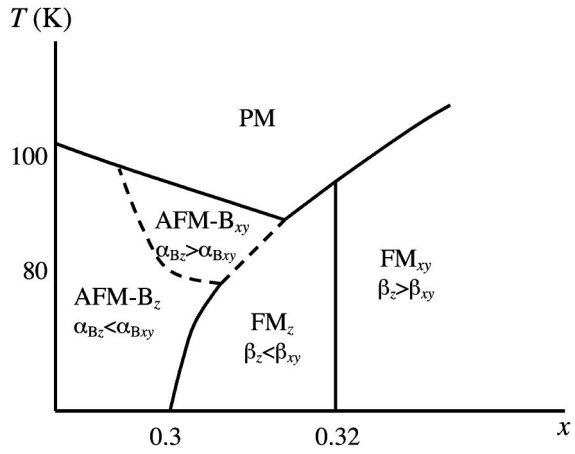

FIG. 1. Schematic phase diagram of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ near $x\sim 0.3$. The subscripts z and xy stand for the easy axis and easy plane, respectively, for the magnetic moments. The dashed lines represent coexistent regions. The anisotropy coefficients α and β are assumed to be positive.

hypothetic phase diagram, Fig. 1, for the bilayered manganites doped near $x=0.3$. The unexpectedly complicated phase diagram contains five phases among which the two pairs of AFM-*B* and FM phases differ only by their orientation of the magnetic moments as indicated by the subscripts. It can explain all the three contradictory observed scenarios above, provided that the reported doping level has a slight difference. Moreover, it is predicted that there are phase separations, which lead to coexistence of different phases as roughly indicated in Fig. 1 by the dashed lines. Furthermore, CMR of percolation origin may be envisioned since the AFM-*B* phase is insulating.

First we identify the order parameters and their symmetry responsible for the possible magnetic structures. The Mn ions with magnetic moments $\boldsymbol{\mu}_i$ in the $I4/mmm$ structure occupy four positions at $i=1(0,0,z)$, $2(0,0,1-z)$ $(z\sim 0.1)$ and their translation by $\mathbf{t}_0=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, i.e., $(\frac{1}{2},\frac{1}{2},\frac{1}{2}\pm z)$ (see Fig. 2).[16] Following the representation analysis of magnetic structures,[17–19] we define two magnetic vectors

$$\mathbf{M}=\boldsymbol{\mu}_1+\boldsymbol{\mu}_2,$$

$$\mathbf{L}=\boldsymbol{\mu}_1-\boldsymbol{\mu}_2. \tag{1}$$

Then an FM state corresponds to **M** propagating with a wave vectors $\mathbf{k}_\Gamma=(000)$, a bilayered-type AFM-*B* and an *A*-type AFM (intrabilayer AFM but interbilayer FM) state to **M** and

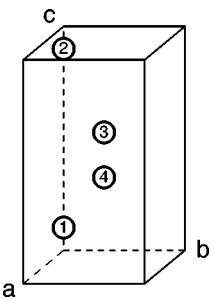

FIG. 2. Elementary unit cell of $I4/mmm$ with four Mn ions and their numbering.

TABLE I. Components of the magnetic vectors that form bases of the IR's of $I4/mmm$ at $\mathbf{k}_\Gamma$ and $\mathbf{k}_M$.

IR	Bases
τ^2	L_z; L_{Az}
τ^3	M_z; L_{Bz}
τ^9	(M_x,M_y); (L_{Bx},L_{By})
τ^{10}	(L_x,L_y); (L_{Ax},L_{Ay})

L propagating, respectively, with $\mathbf{k}_M=(00\frac{1}{2})$ of the first Brillouin zone. Denoting the latter two vectors as $\mathbf{L}_B$ and $\mathbf{L}_A$, respectively, and noticing that $\mathbf{k}_\Gamma$ and $\mathbf{k}_M$ share the same irreducible representations (IR's) of the $I4/mmm$ group,[20] one can find the components of the four vectors that form bases of the IR's shown in Table I. Note that the IR's τ^9 and τ^{10} are both two dimensional, and so M_x and M_y together form a basis vector of τ^9, so do L_{Bx} and L_{By}. From Table I and the possible experimental magnetic structures,[9,11,14] we identify $\mathbf{L}_B$ with the order parameter for the major phase, M_z and (L_{Bx},L_{By}) for the minor phase of $x=0.3$, (M_x,M_y) with the order parameter for $0.3<x\lesssim 0.38$, (M_x,M_y) and (L_{Ax},L_{Ay}) for $0.38<x<0.48$, and (L_{Ax},L_{Ay}) for $0.48\lesssim x<0.5$, which are *A*-type AFM's.

From Table I, the relevant lowest order magnetic part of the Landau free-energy can be written as

$$F=\frac{c}{2}\mathbf{M}^2+\sum_w\frac{a_w}{2}\mathbf{L}_w^2+\sum_w\frac{b_w}{4}\mathbf{L}_w^4+\frac{d}{4}\mathbf{M}^4+\frac{1}{2}\beta_z M_z^2+\frac{1}{2}\beta_{xy}(M_x^2+M_y^2)+\sum_w\left[\frac{1}{2}\alpha_{wxy}(L_{wx}^2+L_{wy}^2)+\frac{1}{2}\alpha_{wz}L_{wz}^2\right], \tag{2}$$

where w represents the summation over **L**, $\mathbf{L}_A$, and $\mathbf{L}_B$. Note that the latter two vectors will carrier a factor $\exp\{-i\mathbf{k}_M\cdot\mathbf{t}_0\}=-1$ when they are translated by $\mathbf{t}_0$ and hence cannot appear in odd powers. In Eq. (2), we have separated the exchange contributions (first four terms), which depend only on the relative orientation of the spins, from the magnetic anisotropic energies (remaining terms), which depend on the relative direction of the magnetic moments to the lattice and arise from the relativistic spin-spin and spin-orbit interactions and so are effects of the order of $O(v_0^2/c_0^2)$, ordinarily about 10^{-2}–10^{-5}, where v_0 is the speed of electrons in the crystal and c_0 that of light, since the magnetic moments themselves contain a factor v_0/c_0.[21] Hence α and β are small constants due to their relativistic origin. b_w and d are positive for stability.

We now consider the AFM-*B* order $\mathbf{L}_B$ at $x=0.3$. Minimizing Eq. (2), one obtains, besides the PM phase with $\mathbf{L}_B=\mathbf{0}$, two additional ordered phases, one, denoted by AFM-B_z as the magnetic moments point to the z axis, with $L_{Bz}^2=-(a_B+\alpha_{Bz})/b$, and the other AFM-$B_{xy}$ with $L_{Bx}^2+L_{By}^2=-(a_B+\alpha_{Bxy})/b$ since the moments lie in the xy plane. As higher-order anisotropic terms like $L_x^2L_y^2$ have not been included, we shall let the direction of the moments in the xy plane be undetermined. Note that the transition points at a_B

$+\alpha_B=0$ of the two phases differ only by the small quantities α_B. Moreover, the difference between their free energies, $-a_B(\alpha_{Bz}-\alpha_{Bxy})/2b_B$ to first order in α_B, is also small. As a result, AFM-B_{xy} is a stable phase if $\alpha_{Bz}>\alpha_{B_{xy}}$ and vice versa, assuming $\alpha>0$ without loss of generality. The two phases have respectively crystallographic space groups $P4/mnc$ and $Cmca$, which cannot be related by an active IR and so the transition between them is necessarily discontinuous.[22] Another reason is that the two directions are not connected continuously.

More importantly, there is no phase with both the z and xy components finite. This is because for a tetragonal lattice, the z and xy components decouple, each carrying an IR of different dimensions (see Table I). Consequently, they are not related to each other, and so both cannot generally acquire nonzero values in a phase transition. Indeed, it can be shown that inclusion of next higher-order mixing terms such as $L_{Bz}^2(L_{Bx}^2+L_{By}^2)$ and $L_{Bx}^2L_{By}^2$, as well as L_{Bz}^4, $(L_{Bx}^2+L_{By}^2)^2$ can only yield real solutions directing along either z axis or xy plane, but not both. Therefore, for a single $\mathbf{L}_B$ order, symmetry does not allow the spins to cant. These results also apply to a single FM order. Thus there are two possible FM phases with different easy axes but close transition temperatures, canting is, however, not allowed.

Nevertheless, canting containing different magnetic vectors is still possible. This may arise from the competition between them, as for example, the competition between double exchange and AFM superexchange, which may be the origin of spin canting around $x=0.4$. Near $x=0.3$, coupling of the type $\mathbf{M}^2\mathbf{L}_B^2$ of either an exchange or a relativistic origin may lead to a canting of the minor phase. However, as such canting involves two different IR's as seen in Table I, a transition from a disordered PM phase should be first order in compliance with Landau's criterion.[22]

We now turn to the experiments to see whether our results help to clarify the controversy near $x=0.3$. We first argue that there is an independent AFM-B_{xy} phase. Consider the detailed analysis by Argyriou *et al.* which gives rise to canting.[11] It is found[11] by high-resolution synchrotron x-ray diffraction that the nominal $x=0.3$ single crystals used in the experiments separate into two chemically distinct phases, the minor phase possessing a slightly higher x value than the major one. For the neutron diffractions, when the planar AFM-B component is negligible at temperature $T=5$ K, the results agree with a mixture of a major AFM-B_z and a minor FM_z phase, whereas at 80 K near which it peaks, if it was exclusively associated with only one phase to produce canting, the resultant total magnetic moment was too large. This is the reason for the assignment of two canting phases with their canting angles varying with temperature.[11] Now noting that a canting AFM-B phase is prohibited, the same reason also excludes the possibility of a canting minor phase *and* a pure AFM-B_z phase. Accordingly, the planar L_{Bxy} reflections should arise at least partly from an independent AFM-B_{xy} phase.

If this is accepted, the controversial observations near $x=0.3$ may be resolved. According to Argyriou *et al.*,[11] as the temperature is lowered, the reflections from the AFM-B_{xy} phase decline accompanying the emergence of those from the FM_z one. This may be viewed as a transition from the former phase to the latter one, in accordance with the results reported by Kubota and co-workers,[13,14] though canting may still be possible, but the peak from the AFM-B_{xy} reflections should be properly accounted for. On the other hand, although Perring *et al.* proposed an AFM-B_z phase,[10] their neutron-diffraction measurements also contain reflections from L_{Bxy} which also peak near 80 K similar to Argyriou's. There are two possibilities as the temperature is further lowered. One is that there is an FM_z phase upon closer inspection of the diffraction data as was done by Argyriou *et al.* Another is that the low-temperature phase is simply AFM-B_z as they reported. The AFM-B_{xy} phase only shows up at intermediate temperatures. The former might be compatible with a possible ''spin flop'' mechanism in which the FM tendency due to double exchange acts as a magnetic field that drive the transition from AFM-B_{xy} to AFM-B_z. At lower temperatures, the double exchange may then be strong enough to align all the spins along the z axis. For the latter possibility, although there is not yet a direct experimental determination of the magnetic structure below $x=0.3$, it has been shown that substitution of a smaller lanthanide ion Nd with La at fixed $x=0.3$ suppresses the FM order.[13] This seems to imply an AFM-B_z phase below $x=0.3$. In this case, the peak may be accounted for by a proper dependence of α_{Bxy} on temperature, leading to a reorientation transition to the other phase.

Combining the above results, and noticing that for $x>0.32$ the FM moments lie in the xy plane,[14] we propose Fig. 1 as a schematic phase diagram near $x=0.3$. There are five phases showing up around that doping, much more complicated than one might expect. The boundaries between the phases are only hypothetic, their exact position rests on further experiments. The gross feature of the phase diagram can be accounted for by a proper assumption on the temperature and doping dependences of quadratic coefficients in Eq. (2). In the following we discuss possible phase separations and percolation implied in Fig. 1.

The dashed lines in Fig. 1 indicate regions of coexistence. There is likely a phase separation between the AFM-B_z and the AFM-B_{xy} phase. It was reported experimentally that coexistence of the AFM-B_z and the FM_z phases arises from a single crystal that is biphasic.[11] Whether different signals come from a monophase or a biphase is controversial.[23] Our theory shows that the transition temperatures of the AFM-B_z and the AFM-B_{xy} phase differ only by the small quantities α_{Bz} and α_{Bxy}. This seems to be borne out by the experiments that the reflections from the two phases start appearing at almost the same temperature.[10,11] Furthermore, from the theory, the two phases then possess close free energies. Accordingly, a small spatial variation of doping or inhomogeneity may make the two phases emerge almost simultaneously at different places. This is the phase separation between the two AFM-B phases, which may possibly be the reason that the L_{Bxy} signals cannot be exclusively associated with the minor FM phase, since at least part of the signals come from the phase separated phase. Reversely, this in turn provides an indirect evidence for the phase separation. At lower temperatures, it is not yet clear whether coexistence of the AFM-B_z phase and the FM_z phase arises from a phase separation similar to the perovskite manganites[19] or from the

reported biphasic behavior,[11] which should still exist at high enough temperatures where phase separation cannot occur.

There should be another coexistence due to a different mechanism between the AFM-B_{xy} phase and the FM_z phase, and is related to percolation mechanism of CMR at this region. It should be noted that a phase with AFM-*B* structures must be insulating, at least along *z* axis. So it is surprising that a familiar CMR peak is observed at the temperature where the AFM-*B* orders emerge,[10] but not below the L_{Bxy} reflection peak, i.e., at the temperature where the FM order becomes detectable.[11] Tunneling as suggested by Kimura *et al.*[3] appears unlikely to produce the peak. Instead, percolation of FM regions seems possible. By adopting a strong-coupling picture between M_z and L_{Bxy}, the transition between them is of first order.[24] Accordingly, regions of FM_z may exist far in the AFM-B_{xy} phase. In the present quasi-two-dimensional system, because of a stronger FM correlation in the layers, percolation through these FM regions is easier to occur, leading to the CMR peak at higher temperatures. So there is a subtle balance among the AFM-B_z, the AFM-B_{xy} and the FM_z phase. Also due to the first-order nature, a remnant AFM-B_{xy} phase resulting from inhomogeneities or supercooling is reasonable, giving rise to the negligible reflections at low temperatures.[11] Further, the strong competition between L_{Bxy} and M_z suppresses the occurrence of the FM_z phase, leading to its substantially lower transition temperature of about 80 K than those of slightly higher doping.[11]

In conclusion, we have analyzed the magnetic structures of the tetragonal bilayered manganites with doping near $x = 0.3$ on the basis of experimental results, as these are basic for understanding the related transport behavior. A prominent result from the symmetry analysis is that the AFM-*B* order near the $x = 0.3$ doping (the major phase[11]) cannot be canting, since it is characterized by a single magnetic vector $\mathbf{L}_B$. From this, a detailed analysis of the controversial experimental results leads to a complicated phase diagram, which contains five magnetic phases near $x = 0.3$. It can consistently account for the observations near this doping. The experimental results also provides an indirect evidence for a phase separation between the AFM-B_z and the AFM-B_{xy} phase, a phase separation between the latter phase and the FM_z phase via a first-order transition between them, and thereby a percolation mechanism for the CMR behavior near $x = 0.3$. Further experimental and theoretical work is highly desirable.

We are grateful to Dr. S. Q. Shen's helpful discussions. This work was supported by a URC fund at HKU.

*Permanent address.

[1] R. M. Kusters, J. Singleton, D. A. Keen, R. Mc Greevy, and W. Heyes, Physica B **155**, 141 (1989); K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, Appl. Phys. Lett. **63**, 1990 (1993); R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993); S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994); F. Zhong, J. M. Dong, and Z. D. Wang, Phys. Rev. B **58**, 15 310 (1998).

[2] Y. Moritomo, A. Asamitsu, H. Kuwahara, and Y. Tokura, Nature (London) **380**, 141 (1996).

[3] T. Kimura, Y. Tomioka, H. Kuwahara, A. Asamitsu, M. Tamura, and Y. Tokura, Science **274**, 1698 (1996).

[4] T. Kimura, A. Asamitsu, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **79**, 3720 (1997).

[5] A. J. Millis, B. I. Shraiman, and R. Mueller, Phys. Rev. Lett. **77**, 175 (1996).

[6] T. G. Perring, G. Aeppli, Y. Moritomo, and Y. Tokura, Phys. Rev. Lett. **78**, 3197 (1997).

[7] D. N. Argyriou, J. F. Mitchell, J. B. Goodenough, O. Chmaissem, S. Short, and J. D. Jorgensen, Phys. Rev. Lett. **78**, 1568 (1997).

[8] R. Osborn, S. Rosenkranz, D. N. Argyiou, L. Vasiliu-Doloc, J. W. Lynn, S. K. Sinha, J. F. Mitchell, K. E. Gray, and S. D. Bader, Phys. Rev. Lett. **81**, 3964 (1998).

[9] K. Hirota, Y. Moritomo, H. Fujioka, M. Kubota, H. Yoshizawa, and Y. Endoh, J. Phys. Soc. Jpn. **67**, 3380 (1998).

[10] T. G. Perring, G. Aeppli, T. Kimura, Y. Tokura, and M. A. Adams, Phys. Rev. B **58**, R14 693 (1998).

[11] D. N. Argyriou, J. F. Mitchell, P. G. Radaelli, H. N. Bordallo, D. E. Cox, M. Medarde, and J. D. Jorgensen, Phys. Rev. B **59**, 8695 (1999).

[12] R. H. Heffner, D. E. MacLaughlin, G. J. Nieuwenhuys, T. Kimura, G. M. Luke, Y. Tokura, and Y. J. Uemura, Phys. Rev. Lett. **81**, 1706 (1998).

[13] Y. Moritomo and M. Itoh, Phys. Rev. B **59**, 8789 (1999).

[14] M. Kubota, H. Fujioka, K. Hirota, K. Ohoyama, Y. Moritomo, H. Yoshizawa, and Y. Endoh, cond-mat/9902288 (unpublished).

[15] Q. A. Li, K. E. Gray, and J. F. Mitchell, Phys. Rev. B **59**, 9357 (1999).

[16] *International Tables for Crystallography*, edited by T. Hahn (Reidel, Boston, 1985), Vol. A.

[17] I. E. Dzyalashinskii, Zh. Éksp. Teor. Fiz. **32**, 1547 (1957) [Sov. Phys. JETP **5**, 1259 (1957)]; **46**, 1420 (1964) [**19**, 960 (1964)].

[18] C. Tolédano and P. Tolédano, *The Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987).

[19] F. Zhong and Z. D. Wang, Phys. Rev. B **60**, 11 883 (1999).

[20] O. V. Kovalev, *Representations of the Crystallographic Space Groups*, edited by H. T. Stokes and D. M. Hatch (Gordon and Breach, Yverson, 1993).

[21] E. M. Lifschitz and L. P. Pitaevski, *Electrodynamics of Continuous Media*, 2nd ed. (Pergamon, Oxford, 1984).

[22] H. T. Stokes and D. M. Hatch, *Isotropy Subgroups of the 230 Crystallographic Space Groups* (World Scientific, Singapore, 1988).

[23] P. D. Battle, M. J. Rosseinsky, and P. G. Radaelli, J. Phys. Soc. Jpn. **68**, 1462 (1999); K. Hirota, Y. Moritomo, H. Fujioka, M. Kubota, H. Yoshizawa, and Y. Endoh, *ibid.* **68**, 1463 (1999).

[24] Y. Imry, J. Phys. C **8**, 567 (1975); F. Zhong and Z. D. Wang, Phys. Rev. B **61**, 3192 (2000).