Persistent photoinduced magnetization and hole droplets in $La_{0.9}Ca_{0.1}MnO_3$ films

H. Huhtinen, R. Laiho, and V. Zakhvalinskii
Wihuri Physical Laboratory, Department of Physics, University of Turku, FI-20014 Finland
(Received 27 January 2005; published 26 April 2005)

Photoinduced magnetization following a stretched exponential growth with time is observed in $La_{0.9}Ca_{0.1}MnO_3$ films exposed to near infrared light in magnetic fields of $B \geqslant 0.1$ mT. The magnetic irreversibility observed below 56 K between zero-field-cooled and field-cooled films is strongly influenced by illumination, giving space to a persistent magnetic state with increased ferromagnetic interactions, modified magnetic anisotropy and decrease of the blocking temperature to 5 K. When the illumination and the magnetic field are removed the magnetization of the films decays very slowly after a short period of fast relaxation but recovers the original level when the field is applied again. Such behavior obeys predictions for domain pinning in narrow-wall random-field Ising systems. The results suggest trapping of photogenerated electrons by magnetic disorder while the holes contribute to growth of ferromagnetism in the films.

DOI: 10.1103/PhysRevB.71.132404 PACS number(s): 75.47.Lx, 75.30.Gw, 75.47.Gk, 75.70.Ak

Ferromagnetism and accompanying metallic conductivity of the hole-doped perovskite manganites $La_{1-x}Ca_xMnO_3$ (LCMO) are conventionally explained by the ferromagnetic (FM) double exchange (DE) mechanism[1] of simultaneous hopping of an e_g electron from $Mn^{3+}(3d^4, t^3_{2g}e^1_g)$ ion on the $O(2p_\sigma)$ orbital and from the $O(2p_\sigma)$ orbital to an empty e_g orbital of $Mn^{4+}(3d^3, t^{3g}_2 e^0_g)$. The magnetic and lattice interactions are coupled by the Jahn-Teller (JT) effect which splits the e_g states of the Mn^{3+} ions. At $x < 0.07$, LCMO is a canted antiferromagnet but for $x < 0.125$, neutron-diffraction[2] and magnetic measurements[3,5] have shown the presence of small ferromagnetic metallic (FM) clusters in a predominantly ferromagnetic insulator (FI) surrounding. This kind of inhomogeneous state is expected to be sensitive to local changes of the hole doping, resulting in rich physical phenomenology. Photoinduced changes of microwave permittivity in low-doped LCMO films have been observed, suggesting an expansion of the FM clusters within the FI phase.[4] Also, resistivity changes have been reported around the Curie temperature of illuminated oxygen-deficient $(La,Ca)MnO_\delta$ films.[5]

In this Brief Report we report observation of persistent photoinduced changes in magnetic properties of LCMO $x = 0.1$ films prepared by pulsed laser deposition on $SrTiO_3$ (100) substrates. Magnetization measurements were made with a SQUID magnetometer applying the field parallel to the plane ($B \perp c$ axis) of a 200-nm-thick circular film ($r = 1.5$ mm) illuminated through an optical fiber with a cw GaAs laser at the wavelength $\lambda = 780$ nm (1.59 eV).

In Fig. 1(a) are shown the temperature dependences of the magnetizations measured in dark after cooling the film in zero magnetic field, $M^{\mathrm{dark}}{}_{\mathrm{ZFC}}(T)$, and in a field of $B = 8$ mT, $M^{\mathrm{dark}}{}_{\mathrm{FC}}(T)$ (filled symbols). These curves deviate below the irreversibility temperature $T_{\mathrm{irr}} = 56$ *K* indicating the inhomogeneous magnetic ground state of LCMO with low x.[2,5] After this the sample was cooled down to 4 K in zero field and illuminated in the field of 8 mT for 15 min at the optical power density of ≈ 25 mW/mm^2. As a result, $M^{\mathrm{ill}}{}_{\mathrm{ZFC}}(T)$ was found to exceed the values of $M^{\mathrm{dark}}{}_{\mathrm{ZFC}}(T)$ and with sufficiently long illumination to reach the $M^{\mathrm{dark}}{}_{\mathrm{FC}}(T)$ curve. Plotting the derivatives $d[M_{\mathrm{ZFC}} - M_{\mathrm{FC}}]/dT$ as a function of temperature, [6] the magnetic blocking temperatures of the film were found to be $T_B = 27$ *K* and $T_B \approx 5$ *K* before and after illumination, respectively. In the inset to Fig. 1(a) are shown the temperature dependences of the photoinduced magnetization differences, $\Delta M(T) = M^{\mathrm{ill}}{}_{\mathrm{ZFC}}(T) - M^{\mathrm{dark}}{}_{\mathrm{ZFC}}(T)$ (squares) and $\Delta M(T) = M^{\mathrm{ill}}{}_{\mathrm{FC}}(T) - M^{\mathrm{dark}}{}_{\mathrm{ZFC}}(T)$ (circles) after prolonged illumination when $M^{\mathrm{ill}}{}_{\mathrm{ZFC}}$ approaches $M^{\mathrm{dark}}{}_{\mathrm{FC}}$. Both plots exhibit a kink at $T_{\mathrm{irr}} = 25$ K signifying the irreversibility temperature of the magnetic phase modified by illumination. On the high temperature side of T_{irr} the values of $\Delta M(T) \propto T^{-1}$ follow the Curie law pertaining to superparamagnetic behavior.[7]

Virgin magnetization curves *M(B)* measured prior and after illumination of the film to near saturation are shown in Fig. 1(b). The difference $M^{\mathrm{ill}} - M^{\mathrm{dark}}$ between the magnetization curves, plotted in the left inset to the figure, has a maximum around 50 mT. As shown in the right inset, the magnetic hysteresis loop is rotated during illumination in comparison with the loop observed in dark and has a lower coercive field. These results give evidence for photoinduced changes of the magnetic anisotropy field, presumably due to growth of the FM phase at expense of the FI phase.[4] These phases have been reported to have different easy magnetization directions.[8]

Provided that the illumination is carried out in a field of $B > 0.1$ mT a *persistent photoinduced magnetization* (PPM) state is observed in our films. In the PPM state, the induced excess magnetization persists a long time after switching off the light. As shown in Fig. 2 the dependence of the *growth of* PPM on the illumination time t obeys a stretched exponential law

$$M^{\mathrm{ill}}(t) = M^{\mathrm{ill}}{}_{\mathrm{sat}} \exp[-(t/\tau)^{\beta}], \tag{1}$$

where $M^{\mathrm{ill}}{}_{\mathrm{sat}}$ is the saturation value of PPM obtained after prolonged illumination and $\tau(B)$ is a characteristic time of the growth of $M^{\mathrm{ill}}(t)$. It is found that $M^{\mathrm{ill}}(B)$ is saturated at B between 15–20 mT and that τ decreases with increasing B obeying an exponential function $\tau(B) = a \exp(bB)$ with a

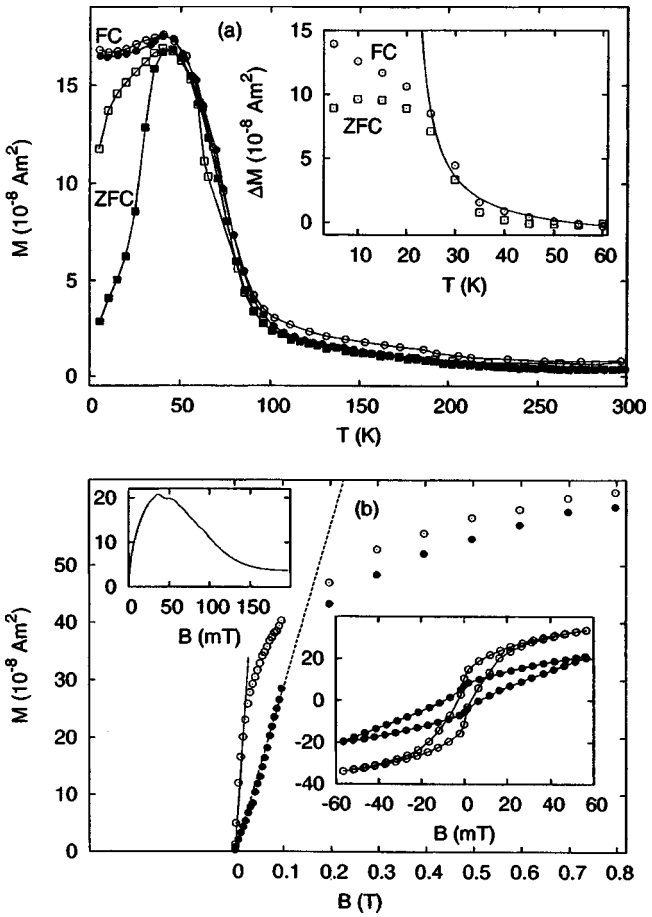

FIG. 1. (a) Temperature dependences of the ZFC and FC magnetizations in a LCMO $x=0.1$ film in a field of 8 mT measured before (■) and after 5 (□) and 15 (○) min of illumination at power density of 25 mw/mm^2. The inset shows the magnetization differences $\Delta M = M^{\mathrm{ill}}{}_{\mathrm{ZFC}}(T) - M^{\mathrm{dark}}{}_{\mathrm{ZFC}}(T)$ (□) and $M^{\mathrm{ill}}{}_{\mathrm{FC}}(T) - M^{\mathrm{dark}}{}_{\mathrm{ZFC}}(T)$ (○). The solid line is a fit to the the Curie law. (b) Virgin curves of the magnetic hysteresis loop measured at 5 K before (●) and after (○) illumination. The left inset shows the difference of these curves in low fields. The right inset shows the complete hysteresis loop at 5 K before (●) and after illumination (○).

$=5.2\times10^3$ *s* and $b=-0.23/\mathrm{mT}$. The stretching exponent β is practically independent of *B* and agrees well with the value of $\beta=0.43$ predicted for charge transfer processes in presence of randomly distributed traps.[9]

The *relaxation of* PPM is shown in Fig. 3(a). When applying a field of 20 mT at $T=5$ K (point 0) the magnetization in dark rises to point 1. Illuminating the film as described above increases the magnetization [following Eq. (1)] from point 1 to point 2. Then both the illumination and the magnetic field are switched off and the relaxation of the remanent magnetic moment $M^{\mathrm{ill}}{}_{\mathrm{rem}}$ is recorded at several constant temperatures. Immediately after removing the field the relaxation is faster than could be measured (start-up time of the magnetometer is ~2 min) but after this period $M^{\mathrm{ill}}{}_{\mathrm{em}}$ remains at an elevated level depending on *T* without practically showing any further relaxation. Only at 5 K the fast relaxation component was small enough so that a fit shown in Fig.

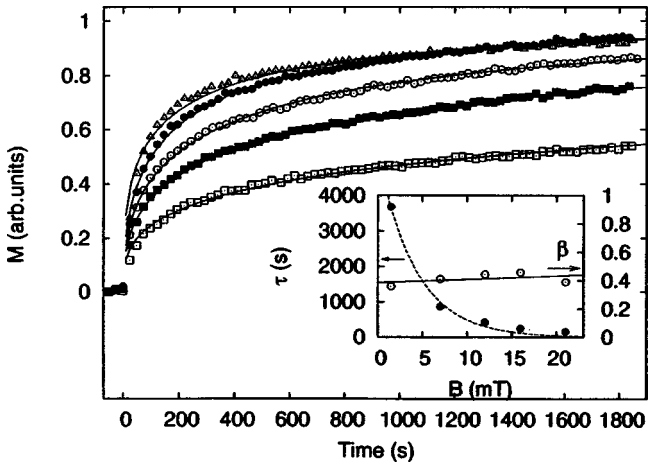

FIG. 2. Time dependence of the growth of the photoinduced magnetization in the LCMO $x=0.1$ film at 10 K and $B=-1.5$ mT (□), −7 mT (■), −12 mT (○), −16 mT (●) and −21 mT (△). The ligh power density is 0.3 mW/mm^2. The inset shows the magnetic field dependence of the characteristic growth time τ and the stretching exponent β obtained from the fit of the data to Eq. (1).

3(b) could be made with a stretched exponential like expression with $\beta\sim0.3$. The relaxation curve at $T=40$ K is shown for comparison. The relatively small contribution of the fast relaxation at 5 K reflects the blocking behavior of the clusters formed under illumination in the film. This temperature agrees well with $T_B=5$ K determined from the temperature derivatives of the difference $M^{\mathrm{ill}}{}_{\mathrm{ZFC}}$—$M^{\mathrm{ill}}{}_{\mathrm{FC}}$ above. When the magnetic field is turned on after relaxation at any temperature between 5–50 K the magnetization in dark attains the level 2 obtained earlier by illumination. This memory effect shows that the photoinduced structures are preserved during relaxation of M^{ill}.

LCMO and LSMO ($S=$Sr) have two broad absorption bands in the near infrared and visible regions, one around 1.5–1.7 eV and the other around 3.1–3.5 eV. Some authors[10,11] assign the 1.5 eV band to *d-d* (Mn) transitions and the 3.5 eV band to $2p(O)\rightarrow3d$(Mn) charge transfer (CT) excitations while others, (LSMO)[12] and (LCMO)[13] ascribe both bands to the 2*p*-3*d* transitions. The minimum optical CT gap Δ_{pd} of $LaMnO_3$ is due to the 2*p*-3*d* excitations at about 1 eV (Refs. 14,15) and in recent one-center molecular orbital calculations it was ascribed to the O $2p(t_{1g})$ $\rightarrow$ Mn $3d(e_g,t_{2g})$ transitions of the MnO_6 center.[16] Strong hybridization of the Mn 3*d* and O 2*p* orbitals have been observed by electron spectroscopic investigations in LCMO $x=0.3$ (Ref. 17) and in LSMO with $x=0.1$.[18] Due to hybridization a smooth redistribution of the hole density from the cations to the anions, depending on the value and the sign of Δ_{pd}, is possible[19] and instead of d^np^6 one would have a predominantly $d^{n+1}p^5$ ground state with spin $\sigma=1/2$ at the oxygen site. In terms of the *p-d* hybridization matrix element t_{pd} this is expected to increase the alignment of the Mn spins via the exchange interaction $J_{\mathrm{Mn\text{-}Mn}}\sim t^4{}_{pd}/|\Delta_{pd}|^3$ which is much stronger than $J_{\mathrm{Mn\text{-}O}}\sim t^2{}_{pd}/|\Delta_{pd}|$.[3,20,21]

In LCMO $x=0.1$ the hole-carrying Mn^{3+}-O-Mn^{4+} complexes are in average much more rare than the Mn^{3+}-O-Mn^3 complexes. To attain the PPM state the photoexcited

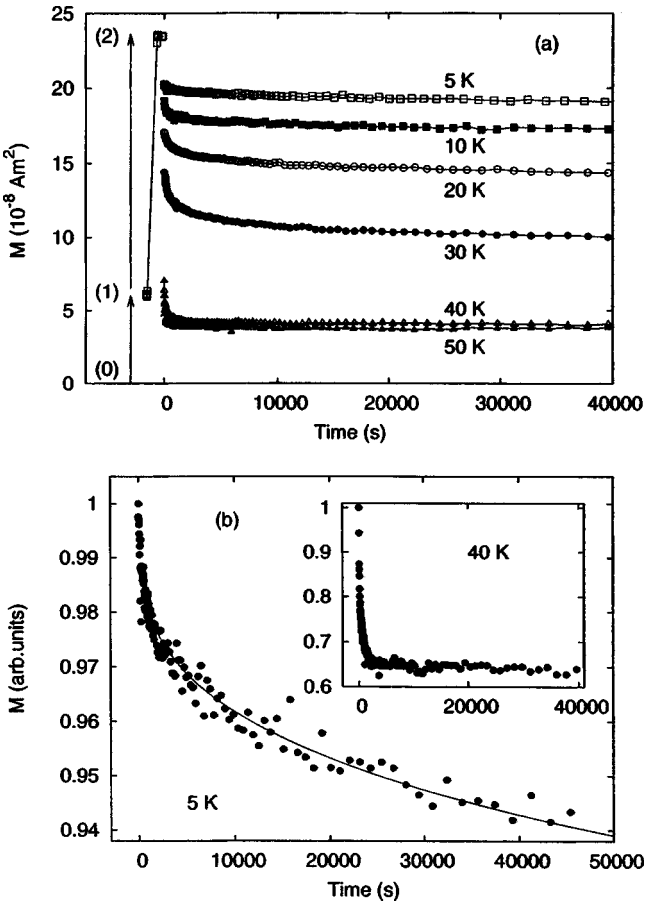

FIG. 3. (a) Relaxation of the photoinduced PPM state in the LCMO $x=0.1$ film. Level 0 gives the magnetization value at $B=0$ (background); level 1 is the magnetization in dark when the field of 20 mT is applied and level 2 the magnetization observed after illumination in that field as in (a). After removing the field at level 2 the relaxation curves at $T=5$ K (□), 10 K (■), 20 K (○), 30 K (●), 40 K (△), and 50 K (▲) are observed.

electron must be self-trapped, e.g., by magnetic disorder while the hole is contributing to magnetic interactions. This is supported by the fact that the characteristic growth time of the PPM decreases strongly with increasing B (see inset to Fig. 2) and that the PPM effect was never observed in our films at $T>T_{\mathrm{irr}}$, i.e., when the efficiency of the magnetic disorder becomes weak due to weakening of the ferromagnetism. This mechanism resembles that of photoinduced persistent superconductivity in low-doped $YBa_2Cu_3O_x$ where the excited electrons are believed to be trapped at oxygen vacancies.[22] Because the hole localization length in the manganites can be of the order of several unit cell lengths a polarized system of hybridized Op-Mn holes and optically excited holes may be formed. It has been suggested using the Kondo p-d model that with two nonfilled shells, Mn3d and O2p, that with further hole doping an insulator-anionic oxygen metal transition and ferromagnetic ordering of O and Mn sublattices should occur.[23] Our observations of the PPM state in LCMO showing stronger ferromagnetism, increase of the metallic phase, changes in the magnetic anisotropy field as well as the low blocking temperature T_B indicating strong ferromagnetic fluctuations pertinent to systems of a few particles are all in line with the predictions in Ref. 23.

The photoinduced magnetization and insulator-to-metal transition reported for heavily doped $Pr_{0.7}Ca_{0.3}MnO_3$ single crystals[24] and thin films of Cr-doped $Pr_{0.5}Ca_{0.5}MnO_3$ (Ref. 25) and $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ (Ref. 26) have been attributed to photocarrier-mediated collapse of the charge-ordered (CO) state into a FM state. Our LCMO with $x=0.1$ is expected to be in the low-temperature CO FI phase[27] embodying ferromagnetic clusters which can contain several holes and start to coalesce between $x=0.08$ and 0.1.[28] It has been suggested that such inhomogeneous state may include metallic hole-rich walls forming stripe structures.[29] When after the long-time relaxation in zero magnetic field [Figs. 3(a) and 3(b)] the field is turned on, $M^{\mathrm{ill}}_{\mathrm{rem}}$ is restored completely to the level observed after illumination (the memory effect above). Such behavior is in agreement with prediction for relaxation of narrow-wall Ising systems[30] and is experimentally observed also for the magnetic model systems $Fe_{0.7}Mg_{0.3}Cl_2$ and $Fe_{0.47}Zn_{0.53}F_2$.[31]

To conclude, we have observed photoinduced persistent magnetization obeying a stretched exponential growth rate in low-doped $La_{0.9}Ca_{0.1}MnO_3$ films illuminated in a weak magnetic field at a low temperature. The slow dynamics of the PPM state suggests trapping of photoexcited electrons by local magnetic disorder in the film providing a rote for persistent electron hole separation. The nontrivial magnetic behavior, including anomalously strong ferromagnetic interactions and fluctuations, are attributed to accumulation of the holes and related growth of narrow FM domains in the illuminated film. Such view is supported by long-time relaxation of the PPM state which resembles the prediction for random-field Ising systems, including FC frozen domain configuration at low temperatures when the external field is switched off. Detailed theoretical analysis assuming the holes predominantly on O2p and/or Mn3d orbitals and their interaction with Mn3d electrons is necessary for deeper understanding of the correlated electron and hole centers in the manganites.

We acknowledge the Wihuri Foundation, Finland, for support.

[1] C. Zener, Phys. Rev. **81**, 440 (1951).

[2] M. Hennion, F. Moussa, J. Rodriguez-Carvajal, L. Pinsard, and A. Revolevschi, Phys. Rev. Lett. **81**, 1957 (1998)].

[3] R. Laiho, E. Lähderanta, J. Salminen, K. G. Lisunov, and V. Zakhvalinskii, Phys. Rev. B **63**, 094405 (2001).

[4] H. Huhtinen, R. Laiho, E. Lähderanta, L. S. Vlasenko, M. P. Vlasenko, and V. S. Zakhvalinskii, Phys. Rev. B **62**, 11 614 (2000).

[5] J. Hao, Guogeng He, Dexing Lu, and Hong-Kuen Wong, Mater. Lett. **46**, 225 (2000).
[6] J. C. Denardin, A. L. Brandl, M. Knobel, P. Panissod, A. B. Pakhomov, H. Liu, and X. X. Zhang, Phys. Rev. B **65**, 064422 (2002).
[7] D. J. Crangle, *Solid State Magnetism* (Edward Arnold, London, 1991), Chap. 6.
[8] W. Markovich, I. Puzniak, D. A. Shulyatev, and Y. M. Mukovskii, Phys. Rev. B **65**, 144402 (2002).
[9] J. C. Phillips, Physica C **340**, 292 (2000); J. C. Phillips, Rep. Prog. Phys. **59**, 1133 (1996).
[10] J. F. Lawler, J. G. Lunney, and J. M. D. Coey, Appl. Phys. Lett. **65**, 3017 (1994).
[11] J. H. Jung, K. H. Kim, T. W. Noh, E. J. Choi, and J. Yu, Phys. Rev. B **57**, R11 043 (1998).
[12] S. Yamaguchi, Y. Okimoto, K. Ishibashi, and Y. Tokura, Phys. Rev. B **58**, 6862 (1998).
[13] Ahmed I. Lobad, A. J. Taylor, C. Kvon, S. A. Trugman, and T. R. Gosnell, Chem. Phys. **251**, 227 (2000).
[14] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).
[15] T. Arima, Y. Tokura, and J. B. Torrance, Phys. Rev. B **48**, 17 006 (1993).
[16] A. S. Moskvin, Phys. Rev. B **65**, 205113 (2002).
[17] R. Zaleski, A. Kolodziejczyk, Cz. Kapusta, and K. Krop, J. Alloys Compd. **328**, 175 (2001).
[18] M. Abbate, F. M. F. Groot, J. C. Fuggle, A. Fujimori, O. Strebel, F. Lopez, M. Domke, G. Kaindl, G. A. Sawatzky, M. Takano, Y. Takeda, H. Eisaki, and U. Uchida, Phys. Rev. B **46**, 4511 (1992).
[19] A. Chainani, M. Mathew, and D. D. Sharma, Phys. Rev. B **47**, 15 397 (1993).
[20] Amnon Aharony, R. J. Birgenau, A. Coniglio, M. A. Kastner, and H. E. Stanley, Phys. Rev. Lett. **60**, 1330 (1988).
[21] D. I. Khomskii and G. A. Sawatzky, Solid State Commun. **102**, 87 (1997).
[22] V. I. Kudinov, I. L. Chaplygin, A. I. Kirilyuk, N. M. Kreines, R. Laiho, E. Lähderanta, and C. Ayache, Phys. Rev. B **47**, 9017 (1993).
[23] A. S. Moskvin and I. L. Avvakumov, Physica B **322**, 371 (2002).
[24] K. Miyano, T. Tanaka, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **78**, 4257 (1997).
[25] Y. Okimoto, Y. Ogimoto, M. Matsubara, Y. Tomioka, T. Kageyama, T. Hasegawa, H. Koinuma, M. Kawasaki, and Y. Tokura, Appl. Phys. Lett. **80**, 1031 (2002).
[26] P. Aleshkevych, M. Baran, R. Szymczak, H. Szymczak, V. A. Bedarev, V. I. Gapon, S. L. Gnatchenko, O. Yu. Gorbenko, and A. R. Kaul', Low Temp. Phys. **30**, 948 (2004).
[27] S.-W. Cheong and H. Y. Hwang, *Colossal Magnetoresistance Oxides*, edited by Y. Tokura (Gordon and Breach, Amsterdam, 2000) p. 238.
[28] G. Biotteau, M. Hennion, F. Moussa, J. Rodríguez-Carvajal, L. Pinsard, A. Revolevschi, Y. M. Mukovskii, and D. Shuulyatev, Phys. Rev. B **64**, 104421 (2001).
[29] G. Papavassiliou, M. Pissas, M. Belesi, M. Fardis, J. Dolinsek, C. Dimitropoulos, and J. P. Ansermet, Phys. Rev. Lett. **91**, 147205 (2003).
[30] T. Natterman and I. Vilfan, Phys. Rev. Lett. **61**, 223 (1988).
[31] U. A. Leitão, W. Kleemann, and I. B. Ferreira, Phys. Rev. B **38**, 4765 (1988); P. Pollak, W. Kleemann, and D. P. Belanger, *ibid.* **38**, 4773 (1988).