PHYSICAL REVIEW B **72**, 233405 (2005)

Out-of-equilibrium electronic transport properties of a misfit cobaltite thin film

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(Received 13 September 2005; published 14 December 2005)

We report on transport measurements in a thin film of the 2D misfit Cobaltite $Ca_3Co_4O_9$. Dc magnetoresistance measurements obey the modified variable range hopping law expected for a soft Coulomb gap. When the sample is cooled down, we observe large telegraphiclike fluctuations. At low temperature, these slow fluctuations have non-Gaussian statistics and are stable under a large magnetic field. These results suggest that the low temperature state is a glassy electronic state. Resistance relaxation and memory effects of pure magnetic origin are also observed, but without aging phenomena. This indicates that these magnetic effects are not glassylike and are not directly coupled to the electronic part.

DOI: 10.1103/PhysRevB.72.233405 PACS number(s): 73.50.−h, 73.23.−b, 72.20.My, 72.70.+m

Layered cobaltites have recently received a growing interest due to their interesting properties. Their rather low resistivity and large Seebeck coefficient at high temperature lead to interesting thermoelectric properties.[1] Superconductivity has been also observed in Na_xCoO_2, yH_2O.[2] From a more fundamental point of view, different interesting points have been noted. For example, specific heat evidences a large effective mass in the $(Na,Ca)Co_2O_4$ family,[3] a good indication of strongly correlated electronic properties. Strong electronic correlations were also recently reported in $Ca_3Co_4O_9$ using electronic transport measurements under pressure.[4] $Ca_3Co_4O_9$ is a misfit incommensurate layered system, with small modulated atomic positions in each layer ($[CoO_2]$ and $[Ca_2CoO_3]$).[5] Furthermore, there is a possibility of frustrated magnetic interactions in a kagome lattice in the CoO_2 layers.[6] Ferrimagnetic or very weak ferromagneticlike properties are also observed at low temperature.[7] In addition, μ^+SR experiments have been interpreted with the presence of a spin density wave at low temperature,[8] giving a clue for a gap opening near the Fermi level leading to the observed "Fermi liquid"-insulator transition. Nevertheless, the low-temperature transport behavior is not really understood, especially because the ground state of the system is quite complex. The eventual link between all these observations and the measured transport properties has to be clarified. The above-mentioned results suggest that low dimensionality, frustration, and disorder, together with strong electronic correlations, can be important features for the physical properties of the $Ca_3Co_4O_9$ system. Since they are known to reinforce fluctuations and metastability, one can expect a strong influence on the transport properties. To our knowledge, this has not been verified by the usual macroscopic transport measurements. Because of the statistical averaging, the discrete nature of the underlying "mesoscopic" processes can be masked in a bulk sample but revealed in a small-area system. In this case, the transport measurements can be used as an efficient probe to bring some light on the ground states of the system.[9]

In this paper, we report a study of dc magnetotransport properties and of resistance fluctuations in a microbridge of a $Ca_3Co_4O_9$ thin film at low temperature. We particularly focus on the origin (magnetic or electronic) of these resistance fluctuations and relaxation.

A 2000 Å epitaxial thick film of $Ca_3Co_4O_9$ was used for the measurements. The film was deposited on (0001) Al_2O_3 using the pulsed laser deposition technique. The details of the optimization, growth conditions, and structural characterizations have been described previously.[10] Prior to the transport measurements, a silver layer was firstly deposited via thermal evaporation onto the film, and secondly a gold layer via rf sputtering. Microbridges ($L=200\ \mu\text{m}\times W=50\ \mu\text{m}$) were then patterned with UV photolithography and argon ion etching. Thin aluminum contact wires were finally used to connect the areas to the electrodes with a wire bonding system. Measurements were made with the four probes method. For the following results, a maximum of 100 nA low noise current was used and any significant current dependence for low current was observed, i.e., quasi-linear response conditions were utilized. The magnetic field was applied along the c axis of the film, perpendicular to the substrate plane.

As it is observed in bulk samples, the $Ca_3Co_4O_9$ film exhibits both a strong increase of the resistance and a large negative magnetoresistance at low temperature[11] (we measure $\Delta R/R \gtrsim -0.6$ at 14 T and 2 K). The analysis of the transport properties in this low temperature part is the main goal of this experiment. One of the most observable characterizations of a localized electronic state is the functional form of the dc resistance. A simple activated law does not describe the data, but a variable range hopping (VRH) expression of the form $R=R_0\exp(T^*/T)^\mu$ ($\mu<1$) gives a very good fit (Fig. 1) for a large temperature range (2 K to 90 K). Interestingly, one finds a much better agreement using $\mu=\frac{1}{2}$ than using the other exponents $\left(\frac{1}{3},\frac{1}{4}\right)$ which can be expected for the Mott VRH regime.[12] This value has been confirmed by analyzing the so-called Zabrodski plot.[13] This latter consists in plotting $\log[\partial\ln R/\partial\ln(1/T)]$ as function of $\log(T)$, the slope of which gives $\mu=0.47\pm0.02$ with a robust precision and mainly without any presupposition on the form of $R(T)$. The exponent $\mu=\frac{1}{2}$ is the most ordinary signature of a soft Coulomb gap in the density of states (the Efros-Shklovskii or ES gap),[14,15] meaning that strong Coulomb (electron-electron) interactions are present. Theory predicts $T^*=Ae^2/(k_B 4\pi\varepsilon_0\kappa\xi)$ (k_B is the Boltzmann constant, ε_0 is the permittivity of the air, κ is the relative dielectric constant, $A=2.8$ and 6.2 for respectively 3D (Ref. 15) and 2D (Ref. 16) systems, and ξ is the localization length). This approach is a single-particle approach and neglects the correlated mo-

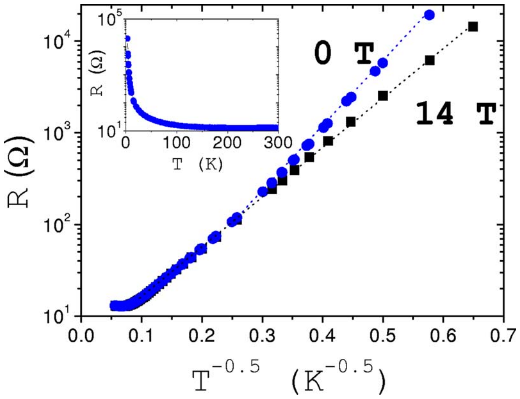

FIG. 1. (Color online) Semilog plot of the resistance as function of $1/\sqrt{T}$, for $B=0$ and 14 T. Linearity in this scale relies on a variable range hopping regime with a Coulomb gap. Inset: Resistance as function of the temperature in a semi-log scale for $B=0$ T.

tion of the charges. It was found from numerical simulations that correlation effects on the carrier's motion relies essentially on a decrease of A ($A\approx 0.61$ was found for the 2D case in a small system). One of the principle merits of this result is to reconcile the introduction of many electron configurations with an unchanged functional form of the ES-VRH,[17] but this shows that there is a large uncertainty on A. From the data at $B=14$ T, we get $T^{*}=159$ K from $T=2$ K to about 90 K. $\kappa\xi\approx 62$ and 640 nm for $A=0.61$ and 6.2, respectively, can be deduced. κ is to our knowledge unknown for $Ca_3Co_4O_9$, but considering $\kappa\approx 10$ as rough approximation, reasonable ξ values can be deduced. Exactly the same analysis was applied to the zero field curve from $T=90$ K up to $T=T_0\approx 15$ K. For $T\leq T_0$, a large negative magnetoresistance is present. This reflects in a slight increase of the exponent μ (0.56±0.02 with the Zabroski plot). This indicates a small departure from a pure parabolic form of the Coulomb gap.[18] However, the most significant feature is the change of T^{*}. This is this change, from $T^{*}=159$ K for $B=14$ T to $T^{*}=267$ K for $B=0$ T, which gives the weight to the observed negative magnetoresistance. Note that since μ does not change significantly for our large magnetic fields range, this means that the electronic interactions keep dominant with no sign of a magnetic hard gap at least for $T\gtrsim 2$ K. Unlike in the 1D cobaltite $Ca_3Co_2O_6$,[19] the Coulomb gap seems to be robust to a high magnetic field. We suggest thus that the magnetoresistance effect comes principally from orbital, rather than spin, effect.[21] This agrees also with the

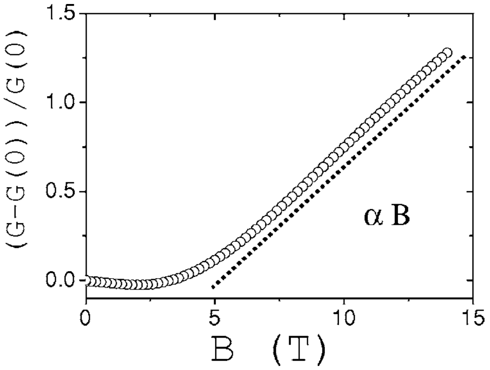

FIG. 2. Normalized magnetoconductance at $T=4.2$ K. Note the small negative magnetoconductance for $B\lesssim 3$ T followed by the strong positive magnetoconductance. The dotted line is a guide to the eyes.

linear field dependence of the magnetoconductance at intermediate fields (Fig. 2).[22] Nevertheless, this point clearly deserves more attention, with a systematic study of the magnetoresistance as a function of the magnetic field orientation. Concerning the dc properties, it can be noted that simple activated form, together with transport nonlinearities usually associated with a spin density waves condensation and their collective depinning,[20] have not been observed.

We will now focus on the time series of the change in resistance. When $T\lesssim 25$ K, large telegraphiclike fluctuations appear. They are generally two-level fluctuations (Fig. 3). The square of the Fourier transform of the time traces gives their spectral representation. After a long acquisition (several hours), we observe a Lorentzian form, meaning that a single characteristic time is sufficient to be statistically representative of the switching process (Fig. 4). The fluctuations are slow, a switcher being in average about 100 s in a resistance state. These characteristic times are only slightly temperature dependent. For high field values (several Tesla), some sequences of three and four levels have been also seen. At 25 K, the first minutes of the resistance traces are dominated by large switches which contribute to the noise, but after some time (typically 1000 s), the noise relaxes to low value. A small perturbation as a 50 G field is enough to destroy the kinetic between the two states [Fig. 3(a)]. Thus, the noisy regime is clearly not really established and the rare events can be thought of precursors of the low temperature state. In strong contrast, at 22.8 K, the noisy regime is robust to a 14 T field [Fig. 3(b)] and is stabilized at least up to several hours, the typical time scale of our longest recording. This

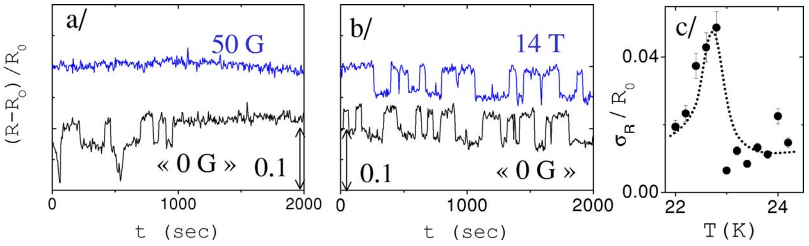

FIG. 3. (Color online) (a) and (b) resistance traces at respectively 25 K and 22.8 K for $B=0$ and 5×10^{-3} T and for $B=0$ and 14 T. The shift of the time traces in each graph is arbitrary. R_0 is the mean value of the resistance averaged during the time of the measurement. (c) The normalized noise versus the temperature. Note the peak of noise at $T=22.9\pm0.1$ K. The dotted line is a guide to the eyes.

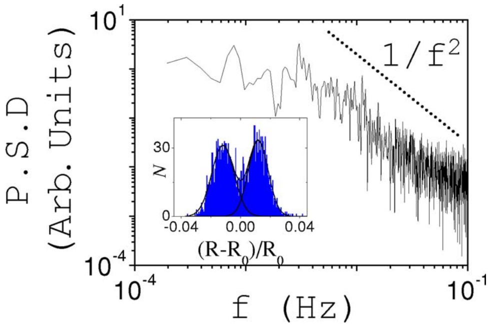

FIG. 4. (Color online) The power spectal density (PSD) corresponding to a very long recording of the time trace at $T=22.80$ K. The well-defined telegraphlike carriers dynamics are evidenced by both the Lorentzian spectrum (corner frequency $f_c \approx 10^{-2}$ Hz) and the bimodal histogram.

indicates a dramatic change on the charge dynamics. This change is confirmed by a peak in the noise value σ_R at a temperature $T=22.9\pm0.1$ K (σ_R corresponds to the integrated noise spectrum over a $10^{-3}-10^{-1}$ Hz bandwidth) [Fig. 3(c)]. This temperature is reasonably separated from T_0, the temperature where the magnetoresistance begins to be measurable. This is a good indication that the noise has not a magnetic origin, in agreement with the small sensitivity to the large magnetic field that has been observed. Correlated hopping conduction should be rather involved, in agreement with the very long time scales associated to the resistance fluctuations.[23]

At the lowest temperatures, a notable change in the fluctuation dynamics, with the appearance of a large intermittence (Fig. 4), is observed. After Fourier transforming and squaring the time traces, the noise spectra are found with a $1/f^{\alpha}$ shape, where α is close to 1.3 (inset of Fig. 5). This contrasts to the Lorentzian shape observed near $T=22.9$ K. We stress also that the observed small temperature dependence of the noise power when the temperature decreases rules out simple thermally activated trapping processes. In addition, it can be realized that the observed intermittence implies that the fluctuations are not stationary anymore. This means that the noise spectrum itself significantly changes with time. This "noise of the noise" can be characterized by the second spectrum $S^2(f)=1/f^{1-\beta}$ introduced in Ref. 24. This corresponds to the fourth-order statistic spectrum of the ordinary $1/f^{\alpha}$ noise. A nonwhite $S^2(f)$ is typical of a non-Gaussian averaging process. If one excludes the case of a dynamic redistribution of the current in an inhomogeneous paths gallery,[25] this implies interacting fluctuators. In practice, the voltage signal was acquired during a very long time (several hours), then segmented, and finally each segment was Fourier transformed and integrated to obtain a time series of noise power. They were taken for different ranges of frequencies and then Fourier transformed, to finally obtain $S_2(f)$. As shown in Fig. 6, this second spectrum is found nearly white at $T=22.8$ K in the telegraphic noise regime. In strong contrast, a large exponent $(1-\beta)\approx 0.9$ is measured at 8 K. We conclude that charge fluctuations are strongly correlated at this moderately low temperature. This behavior is close to what was observed in 2D electronic systems far in the localized regime, at a much lowest temperature.[26] In summary, the low-temperature phase of $Ca_3Co_4O_9$ exhibits glassy electronic transport properties and a Coulomb gap form of the dc conductivity, i.e., can be called a Coulomb glass.

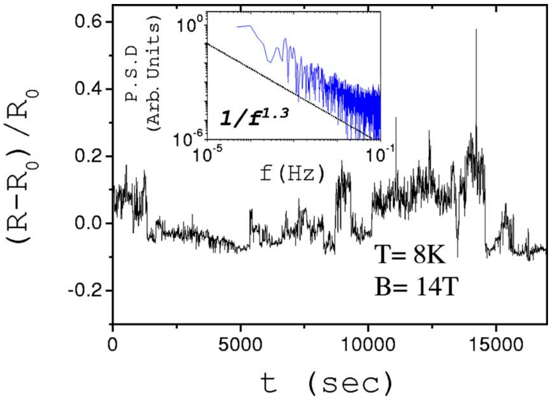

FIG. 5. (Color online) Long time acquisition of the resistance trace at $T=8$ K and $B=14$ T. Inset: The associated Fourier transform with a $(1/f^{1.3})$ form.

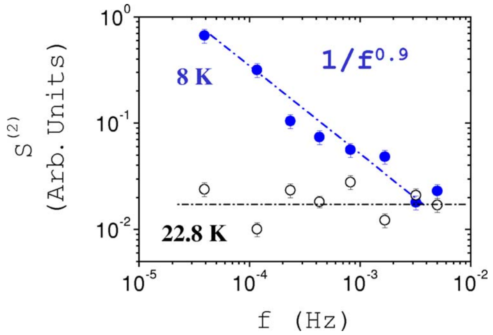

FIG. 6. (Color online) Second spectra $S^2(f)$ of the resistance fluctuations at 22.8 K and 8 K. Correlated fluctuations are evidenced by the nonwhite second spectrum such as measured at the low temperature.

Furthermore, when the sample is cooled down from high temperature to 4 K, the resistance is measured hysteretic when cycling the magnetic field for the first time (Fig. 7). It is reversible after this first cycle and then reveals the equilibrium magnetoresistance properties (Fig. 2). In addition, after a field cooling, the resistance relaxes slowly downwards with time. A simple exponential relaxation gives generally a good fit to the data, and its asymptotic limit after a long time is close to the low resistance state value. Such out-of-equilibrium features can be observed in a very large number of systems which exhibits pinning by disorder, metastability, genuine glassy properties (etc). In the case of $Ca_3Co_4O_9$, the possible frustration of the interactions between spins in the triangular Co lattice degenerates the free energy. This can be a reason for spin glasslike properties as observed, for example, in Kagome lattices.[27] A discriminating test is to check if the system itself evolves with time, i.e., "ages." For that, a standard procedure is started at a temperature T_i and at a field B_i, and then the system evolves with the time t_w. The field is quenched and the resistance is measured during the time t.[28] After this procedure, if aging occurs, the relaxation should

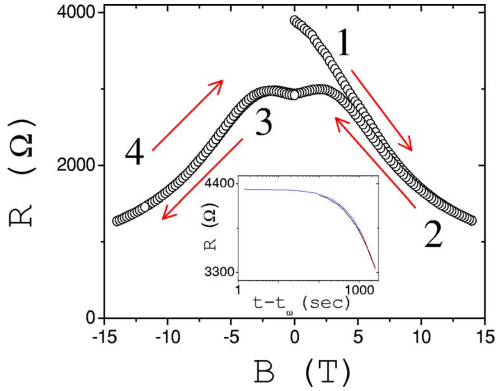

FIG. 7. (Color online) Variation of the resistance as a function of the magnetic field at $T=4$ K after a zero field cooling. Inset: relaxation of the thermo-remanent resistance after a 2 T FC for $t_w=10,100,1000$ s as function of $t-t_w$.

differ for different t_w. A scaling law in t/t_w^{α} provides generally a good fit to the data.[28] In the inset of Fig. 7, it can be observed that the system evolves during the waiting time, but with a relevant rescaling in $t-t_w$. This means that the system relaxes but respects time-translation invariance and that the magnetic out-of-equilibrium state *is not* a spin glass in its proper sense. Nevertheless, a memory of the relaxation after a small temperature change is seen. It is known that similar experimental signatures, namely slow relaxation and memory without aging, are observed when weakly interacting magnetic nanoparticles are present, without the need of a correlation length of a spin-glass order.[29] Thus, we propose an explanation of the relaxation properties in terms of superparamagneticlike relaxation. The associated relaxation time τ^{-1} is maximal at the temperature T_0 where the magnetoresistance has been found to disappear (not shown), confirming the magnetic origin of the relaxation. We propose that short-range ordered clusters of mostly ferromagnetic Co ions are the relevant entities. It is clear that any probe of magnetic correlations at intermediate scales, such as probed by small angle neutron scattering, should be interesting to give more clues on this magnetic ground state.

In summary, we have shown that the low-temperature magnetotransport properties of $Ca_3Co_4O_9$ can be described as a localized state with a Coulomb gap. A non-Gaussian regime of resistance fluctuations is present at moderately low temperature. This can be attributed to correlated charge fluctuations characteristics of an electron glass. An additional field-dependent resistance relaxation is observed but does not show glassy phenomena like aging, and thus is not directly coupled to the pure electronic part.

A.P. would like to acknowledge L. Méchin (GREYC-ENSICAEN) for patterning the microbridges, S. Hébert and Ch. Simon (CRISMAT-ENSICAEN) for critical readings of the paper, and F. Ladieu (SPEC-CEA-SACLAY) for very helpful remarks concerning the slow dynamic of magnetic systems. H.W.E. acknowledges the CNRS and the conseil régional de Basse Normandie for funding.

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[1] S. Hébert, S. Lambert, D. Pelloquin, and A. Maignan, Phys. Rev. B **64**, 172101 (2001).

[2] K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature (London) **422**, 53 (2003).

[3] Y. Ando, N. Miyamoto, K. Segawa, T. Kawata, and I. Terasaki, Phys. Rev. B **60**, 10580 (1999).

[4] P. Limelette, V. Hardy, P. Auban-Senzier, D. Jérome, D. Flahaut, S. Hébert, R. Frésard, Ch. Simon, J. Noudem, and A. Maignan, Phys. Rev. B **71**, 233108 (2005).

[5] D. Grebille, S. Lambert, F. Bourée, and V. Petricek, J. Appl. Crystallogr. **37**, 823 (2004).

[6] W. Koshibae and S. Maekawa, Phys. Rev. Lett. **91**, 257003 (2003).

[7] L. B. Wang, A. Maignan, D. Pelloquin, S. Hébert, and B. Raveau, J. Appl. Phys. **92**, 124 (2002). J. Sugiyama, C. Xia, and T. Tani, Phys. Rev. B **67**, 104410 (2003).

[8] J. Sugiyama, J. H. Brewer, E. J. Ansaldo, H. Itahara, K. Dohmae, Y. Seno, C. Xia, and T. Tani, Phys. Rev. B **68**, 134423 (2003).

[9] M. B. Weissman, Rev. Mod. Phys. **60**, 537 (1988).

[10] H. W. Eng, W. Prellier, S. Hébert, D. Grebille, L. Méchin, and B. Mercey, J. Appl. Phys. **97**, 013706 (2005).

[11] A. C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, and J. Hejtmanek, Phys. Rev. B **62**, 166 (2000).

[12] N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1974).

[13] A. G. Zabrodskii and K. N. Ninov'eva, Zh. Eksp. Teor. Fiz. **86**, 727 (1984) [Sov. Phys. JETP **59**, 425 (1984)].

[14] A. L. Efros and B. I. Shklovskii, J. Phys. C **8**, L49 (1975).

[15] B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductor* (Springer, New York, 1984).

[16] V. L. Nguyen, Sov. Phys. Semicond. **18**, 207 (1984).

[17] A. Pérez-Garrido, M. Ortuño, E. Cuevas, J. Ruiz, and M. Pollak, Phys. Rev. B **55**, R8630 (1997).

[18] M. E. Raikh and I. M. Ruzin, Sov. Phys. JETP **68**, 642 (1989).

[19] B. Raquet, M. N. Baibich, J. M. Broto, H. Rakoto, S. Lambert, and A. Maignan, Phys. Rev. B **65**, 104442 (2002).

[20] G. Grüner, Rev. Mod. Phys. **66**, 1 (1994).

[21] U. Sivan, O. Entin-Wohlman, and Y. Imry, Phys. Rev. Lett. **60**, 1566 (1988); O. Entin-Wohlman, Y. Imry, and U. Sivan, Phys. Rev. B **40**, 8342 (1989).

[22] V. I. Nguyen, B. Z. Spivak, and B. I. Shklovskii, Zh. Eksp. Teor. Fiz. **89**, 1770 (1985) [Sov. Phys. JETP **62**, 1021 (1985)].

[23] J. G. Massey and M. Lee, Phys. Rev. Lett. **79**, 3986 (1997).

[24] P. J. Restle, R. J. Hamilton, M. B. Weissman, and M. S. Love, Phys. Rev. B **31**, 2254 (1985).

[25] G. T. Seidler, S. A. Solin, and A. C. Marley, Phys. Rev. Lett. **76**, 3049 (1996).

[26] S. Bogdanovich and D. Popović, Phys. Rev. Lett. **88**, 236401 (2002); J. Jaroszyński, D. Popović, and T. M. Klapwijk, *ibid.* **89**, 276401 (2002).

[27] F. Ladieu, F. Bert, V. Dupuis, E. Vincent, and J. Hammann, J. Phys.: Condens. Matter **16**, 735 (2004).

[28] E. Vincent, V. Dupuis, M. Alba, J. Hammann, and J. P. Bouchaud, Europhys. Lett. **50**, 674 (2000).

[29] M. Sasaki, P. E. Jönsson, H. Takayama, and H. Mamiya, Phys. Rev. B **71**, 104405 (2005).