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Superpoissonian shot noise in organic magnetic tunnel junctions

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Organic molecules have recently revolutionized ways to create new spintronic devices. Despite intense studies, the statistics of tunneling electrons through organic barriers remains unclear. Here, we investigate conductance and shot noise in magnetic tunnel junctions with 3,4,9,10-perylene-teracarboxylic dianhydride (PTCDA) barriers a few nm thick. For junctions in the electron tunneling regime, with magnetoresistance ratios between 10% and 40%, we observe superpoissonian shot noise. The Fano factor exceeds in 1.5–2 times the maximum values reported for magnetic tunnel junctions with inorganic barriers, indicating spin dependent bunching in tunneling. We explain our main findings in terms of a model which includes tunneling through a two level (or multilevel) system, originated from interfacial bonds of the PTCDA molecules. Our results suggest that interfaces play an important role in the control of shot noise when electrons tunnel through organic barriers. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4903739]

Organic elements in electronic devices have some advantages over inorganic ones, like the ability to chemically adjust their electronic properties, their mechanical flexibility, and the capability to form self-assembled layers. Exploring the unique properties of the organic world to improve and create new functionalities in spin related optics, electronics, and memory elements has been attracting considerable attention in the past decade.[1–7] Organic spintronics may lead to unique devices, for instance, organic light emitting diodes (OLEDs) based on magnetically controlled luminescence.[8] A key limiting factor for the operation of these and related devices is their signal to noise ratio. Thus, the investigation of noise sources in organic tunnel junctions and spin valves is of fundamental and technological interest, as the noise ultimately determines their practical applications.

Low frequency noise and shot noise (SN) measurements have been systematically used to characterize the electronic transport mechanisms in inorganic spintronics.[9–16] On the other hand, noise in organic-based devices, which could have 1/*f* and shot noise contributions, remains poorly understood. For example, 1/*f* noise measurements have been used to determine device quality,[17] or transport features in graphene-based devices (including one or several layers).[18] In another study, the 1/*f* noise and DC leakage measurements were used as a diagnostic tool for OLED reliability in a production line.[19] Current 1/*f* noise measurements have been also used to identify individually contacted organic molecules.[20,21]

Earlier noise measurements in organic spintronic devices were carried out at large applied voltages, where the 1/*f* noise is dominant so the role of shot noise could not be determined. Apart from a technological view, precise knowledge of SN can provide a valuable information on electron correlations near the interfaces with organic barriers, especially in the regime of direct tunneling. In fact, the role of interfaces remains one of the central issues in organic spintronics.[22]

We analyze the tunneling statistics of organic magnetic tunnel junctions (O-MTJs) by measuring shot noise, known to be an excellent tool for investigating the correlations and other details of electron tunneling, well beyond the capabilities of transport measurements.[23–33] Shot noise originates from the discrete nature of charge carriers, therefore, unlike thermal noise, its contribution to low frequency noise survives down to low temperatures. The normalized shot noise (or Fano factor F) indicates[23] whether the tunneling is uncorrelated (poissonian, $F=1$), anti-bunched (sub-poissonian, typically due to negative correlations, $F<1$) or bunched (super-poissonian, typically due to positive correlations, $F>1$).

We have investigated the conductance and shot noise of O-MTJs with PTCDA molecular barriers in the direct tunneling regime.[34] In contrast to MTJs with inorganic barriers,[10,11] tunneling through molecular barriers shows *super-poissonian* shot noise which additionally depends on the relative alignment of the electrodes' magnetization. Our observations are qualitatively accounted for within a model based on spin dependent electron tunneling through an interacting two-level (or multi-level) system.

The layer sequence of the studied O-MTJs is: NiFe(25 nm)/CoFe(15 nm)/AlO_x(0.6 nm)/PTCDA(1.2–5 nm)/AlO_x(0.6 nm)/CoFe(30 nm). The structure was deposited onto a glass substrate, and prepared in a high-vacuum

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environment with a base pressure lower than 10^{-8} mbar. The metallic layers were deposited by sputtering at an Ar working pressure of 5×10^{-3}mbar. The PTCDA layers were grown by thermal evaporation at 10^{-8} mbar, with a deposition rate of 0.1 nm/s. Thin AlO_x buffer layers were grown between the PTCDA layer and both ferromagnetic layers by partially oxidizing Al in oxygen plasma for 5 s. XPS measurements of the Co/PTCDA interface have revealed that the addition of a buffer layer prevents the hybridization between both layers,[35] preserving an effective spin injection into the organic spacer. Figure 1(a) shows a diagram of the investigated O-MTJs. The PTCDA molecules have been found to lie essentially flat over both AlO_x/Co or Co, with a tilt angle of $12° \pm 3°$.[35]

The voltage noise was measured using a cross-correlation technique, described elsewhere.[10,11] The correct calibration of our setup has been confirmed by independent studies.[14,15] The current noise power in the absence of correlations is Poissonian (full shot noise) and is given by $S_I = 2eI$, where I is the average current and e the electron charge. The voltage full SN is then $S_{full} = 2eIR_d^2$, with R_d being the dynamic resistance obtained from the corresponding $I - V$ curves. The experimental SN, S_{exp}, is obtained by fitting a Gaussian peak to the histogram of the part of the spectra independent of frequency (see the supplementary material[36]). The Fano factor F is then calculated as $F = S_{exp}/S_{full}$.

Figure 1(b) shows that the resistance of the junctions increases exponentially with the thickness of the PTCDA barrier. This indicates that the PTCDA layer acts as a barrier in the single-step tunneling regime.[38] Further proof can be found in Ref. 36, where the conductance *vs*. temperature is compared to hopping transport models. Figure 1(c) shows the tunneling magnetoresistance (TMR) for three different temperatures in a 2 nm PTCDA O-MTJ, where the parallel (P) and antiparallel (AP) magnetic alignment of the electrodes are indicated by arrows. The TMR decreases when the bias reaches 100 mV (see Fig. 1(d)). Figure 1(d) also presents the differential conductance in the P and AP states as a function of the bias voltage at T = 0.3 K for a 4 nm PTCDA O-MTJ. We found that the magnetic tunnel junctions with PTCDA barriers were more robust than conventional inorganic MTJs, and typically did not experience dielectrical breakdown as readily. Out of 14 samples studied, only 3 have degraded during multiple bias sweeps up to 500 mV.

The experimental SN and S_{full} and Fano factor at $T = 0.3\,K$ for the 2 nm PTCDA junction from Fig. 1(c) are shown in Figs. 2(a) and 2(b) for the P and AP states. Figs. 2(c) and 2(d) show similar graphs for a sample with a 5 nm thick PTCDA barrier. As can be seen, the F factor ranges from $F = 1$ at low voltages to $F \simeq 2$ at higher voltages. All the O-MTJ samples measured displayed a qualitatively similar variation of the Fano factor with the bias voltage. The shot noise could be obtained for voltages up to a few tens of mV only. The maximum voltage for which the shot noise is measured corresponds to the energy at which the 1/*f* noise becomes dominant and obscures the frequency independent part of the noise spectrum. The spectra could be obtained up to 100 kHz, but a filtering arising from the sample capacitance (dependent on the PTCDA thickness) allowed shot noise measurements only between 1–10 kHz. The appearance of 1/*f* noise restricted SN measurements in all the studied samples, especially in the AP state.

Figure 3(a) presents the average saturation value of the Fano factor in the P state for the samples which presented the frequency-independent spectra. Figure 3(a) also shows the variation of TMR with the PTCDA thickness. Control junctions, with only a 1.2 nm AlO_x layer, show TMRs below 1%, and a metallic-like electron transport (see Ref. 36). This points to diffusive electron transport, for which the theory[23] predicts the Fano factor equal to 1/3. Thus, control measurements prove that the super-poissonian SN is due to the PTCDA barriers. Our O-MTJs with PTCDA thicknesses between 1.2 and 5 nm show relatively high TMR and super-poissonian tunneling statistics with the Fano factor approaching 2, indicative of co-tunneling or tunneling with bunching. Eight O-MTJs of different barrier thicknesses, from four sample sets, have shown qualitatively similar SN values (Fig. 3(a)).

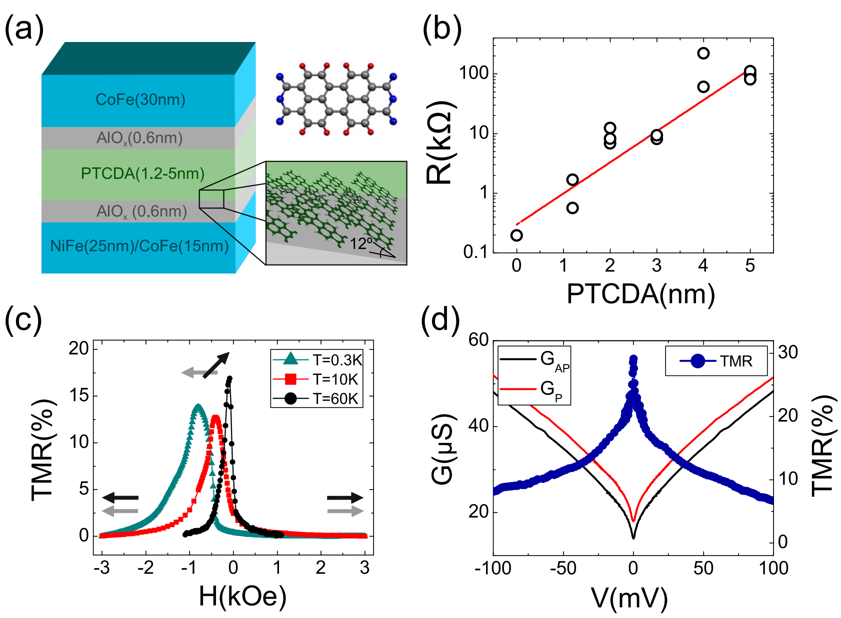

FIG. 1. (a) Sketch of the sample's layered structure. Diagram of the PTCDA molecule.[37] The molecules lay almost in plane, with a 12° tilt angle.[35] (b) Experimental dependence of the resistance on the PTCDA thickness. (c) TMR curves at different temperatures for a sample with 2 nm of PTCDA. (d) Dependence of the TMR and differential conductance on the bias voltage in the P and AP states for a 4 nm PTCDA O-MTJ.

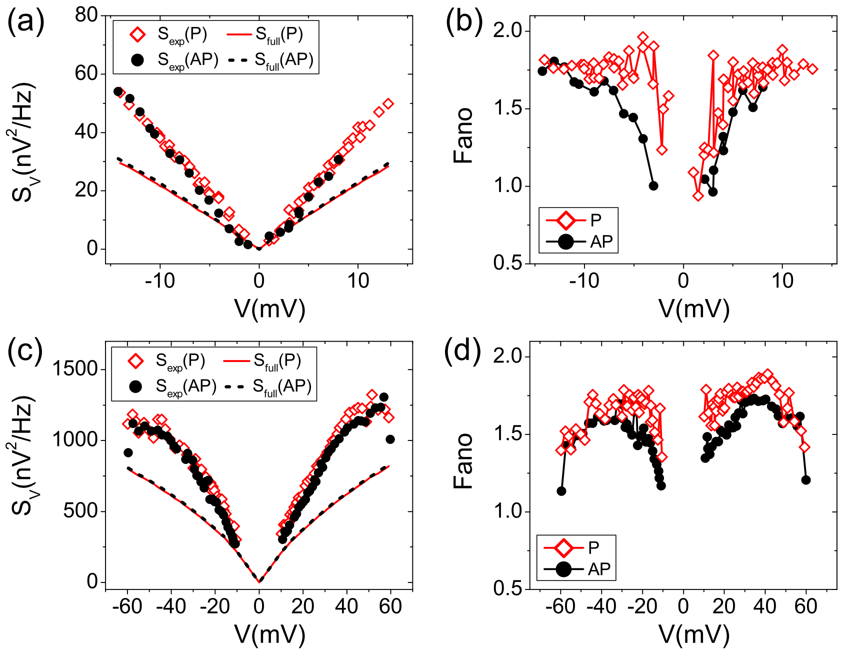

FIG. 2. Voltage dependence of the noise at T = 0.3 K in the P and AP states of the (a) experimental (dots) and expected full shot noise (lines) and (b) Fano factor for a 2 nm PTCDA O-MTJ. (c) and (d) present similar results for a 5 nm PTCDA O-MTJ.

A number of electron tunneling mechanisms (Kondo effect,[39] co-tunneling,[40,41] and others[42,43]) are capable of producing super-poissonian SN, relevant mostly for small quantum dots. Inelastic electron tunneling spectroscopy (IETS) spectra from our samples reveal multiple features (peaks) which could have an electronic and/or vibrational origin (see Ref. 36). The observed SN has been accounted for in terms of the approach developed by Belzig,[29] extended to spin dependent transport. The corresponding model is based on tunneling through a spin dependent, two-level system (or multi-level system in a more general case), with remarkably different tunneling rates. The statistics of the transport process are described as a sum of independent Poissonian events during which a group or "bunch" of n electrons transfer independently.[29] This arises from the difference in tunnel rates between the two levels and the transfer of one or more elementary charges in each process leads to an enhanced noise. Details of the model and description will be presented elsewhere. In Fig. 3(b), we show the calculated (lines) and experimental (points) TMR and Fano factor in the P and AP states as a function of the parameter β, which describes the spin asymmetry in tunneling rates.

Physically, the two or more levels with different couplings can have their origin in localized states arising from interfacial bonds between the PTCDA molecules and the AlO_x buffer layers. The following arguments suggest that the localized states in the model have an interfacial nature: (i) the exponential dependence of the tunneling resistance on PTCDA thickness (Fig. 1(b)) including the metallic character of the conductance when only the AlO_x buffer layer is present (see Ref. 36); (ii) a lateral size of the junctions larger than a micron, for which the influence of Coulomb blockade is minimized. We believe that the main role of the AlO_x layers in the superpoissonian shot noise is providing the two (or multi) levels localized at the AlO_x/PTCDA interface. Therefore, the tunneling process takes place through two parallel channels with statistics controlled by interfacial two-level systems. The origin of the interfacial states could be a charge neutrality level,[44] or gap states,[45] which appear due to the alignment of the energy levels at metal/organic interfaces.[46] The bias dependence of the interfacial density of states could explain the suppression of the Fano factor at large voltages (Fig. 2(b)).

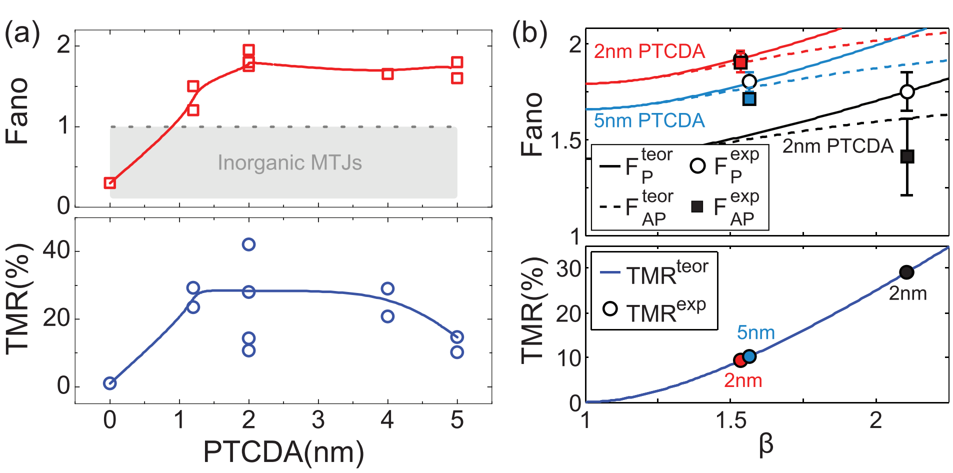

FIG. 3. (a) Maximum Fano factor in the P state and the zero bias TMR *vs* the PTCDA thickness, shown to be well above the range for inorganic barriers. (b) Fit of the theory to experimental values of F and TMR for the samples with 2 and 5 nm of PTCDA. The points are obtained from the average saturation value in the Fano factor *vs* bias plots, and the error bars indicate the dispersion of the average.

In *conclusion*, super-poissonian statistics in tunneling events through the PTCDA molecular barriers have been unveiled by shot noise measurements. A superpoissonian shot noise has been found, which is likely due to localized states originated from interfacial bonds of the PTCDA molecules. For a technological application, the shot noise could be reduced or controlled, for instance, by the growth of double-barrier[47] O-MTJs. Challenges for further work include extending the bias range where the shot noise could be investigated and comparing the role of the organic layers in the superpoissonian SN by the study of O-MTJs with different organic layers.

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[1]V. Dediu, M. Murgia, F. Matacotta, C. Taliani, and S. Barbanera, Solid State Commun. **122**, 181 (2002).
[2]Z. H. Xiong, D. Wu, Z. Valy Vardeny, and J. Shi, Nature **427**, 821 (2004).
[3]A. R. Rocha, V. Garcia-Suarez, S. W. Bailey, C. J. Lambert, J. Ferrer, and S. Sanvito, Nat. Mater. **4**, 335 (2005).
[4]T. S. Santos, J. S. Lee, P. Migdal, I. C. Lekshmi, B. Satpati, and J. S. Moodera, Phys. Rev. Lett. **98**, 016601 (2007).
[5]S. Sanvito, Chem. Soc. Rev. **40**, 3336 (2011).
[6]J. S. Jiang, J. E. Pearson, and S. D. Bader, Phys. Rev. Lett. **106**, 156807 (2011).
[7]R. Vincent, S. Klyatskaya, M. Ruben, W. Wernsdorfer, and F. Balestro, Nature **488**, 357 (2012).
[8]T. D. Nguyen, E. Ehrenfreund, and Z. V. Vardeny, Science **337**, 204 (2012).
[9]E. R. Nowak, R. D. Merithew, M. B. Weissman, I. Bloom, and S. S. P. Parkin, J. Appl. Phys. **84**, 6195 (1998).
[10]R. Guerrero, F. G. Aliev, Y. Tserkovnyak, T. S. Santos, and J. S. Moodera, Phys. Rev. Lett. **97**, 266602 (2006).
[11]R. Guerrero, D. Herranz, F. G. Aliev, F. Greullet, C. Tiusan, M. Hehn, and F. Montaigne, Appl. Phys. Lett. **91**, 132504 (2007).
[12]J. Scola, H. Polovy, C. Fermon, M. Pannetier-Lecoeur, G. Feng, K. Fahy, and J. M. D. Coey, Appl. Phys. Lett. **90**, 252501 (2007).
[13]J. M. Almeida, P. Wisniowski, and P. Freitas, IEEE Trans. Magn. **44**, 2569 (2008).
[14]K. Sekiguchi, T. Arakawa, Y. Yamauchi, K. Chida, M. Yamada, H. Takahashi, D. Chiba, K. Kobayashi, and T. Ono, Appl. Phys. Lett. **96**, 252504 (2010).
[15]T. Arakawa, K. Sekiguchi, S. Nakamura, K. Chida, Y. Nishihara, D. Chiba, K. Kobayashi, A. Fukushima, S. Yuasa, and T. Ono, Appl. Phys. Lett. **98**, 202103 (2011).
[16]T. Tanaka, T. Arakawa, M. Maeda, K. Kobayashi, Y. Nishihara, T. Ono, T. Nozaki, A. Fukushima, and S. Yuasa, Appl. Phys. Lett. **105**, 042405 (2014).
[17]N. Clément, S. Pleutin, O. Seitz, S. Lenfant, and D. Vuillaume, Phys. Rev. B **76**, 205407 (2007).
[18]A. A. Balandin, Nat. Nanotechnol. **8**, 549 (2013).
[19]P. Rocha, H. Gomes, L. Vandamme, D. De Leeuw, S. Meskers, and P. van de Weijer, in *22nd International Conference on Noise and Fluctuations (ICNF)* (IEEE, 2013), pp. 1–4.
[20]M. Tsutsui, M. Taniguchi, and T. Kawai, Nat. Commun. **1**, 138 (2010).
[21]J. Schaffert, M. Cottin, A. Sonntag, H. Karacuban, C. Bobisch, N. Lorente, J.-P. Gauyacq, and R. Muller, Nat. Mater. **12**, 223 (2012).
[22]T. Keevers, A. Danos, T. Schmidt, and D. McCamey, Nat. Nanotechnol. **8**, 886 (2013).
[23]Y. Blanter and M. Bttiker, Phys. Rep. **336**, 1 (2000).
[24]B. R. Bułka, J. Martinek, G. Michałek, and J. Barnaś, Phys. Rev. B **60**, 12246 (1999).
[25]Y. Tserkovnyak and A. Brataas, Phys. Rev. B **64**, 214402 (2001).
[26]R. López and D. Sánchez, Phys. Rev. Lett. **90**, 116602 (2003).
[27]A. Thielmann, M. H. Hettler, J. König, and G. Schön, Phys. Rev. B **68**, 115105 (2003).
[28]A. Cottet, W. Belzig, and C. Bruder, Phys. Rev. Lett. **92**, 206801 (2004).
[29]W. Belzig, Phys. Rev. B **71**, 161301 (2005).
[30]F. M. Souza, A. P. Jauho, and J. C. Egues, Phys. Rev. B **78**, 155303 (2008).
[31]A. L. Chudnovskiy, J. Swiebodzinski, and A. Kamenev, Phys. Rev. Lett. **101**, 066601 (2008).
[32]F. G. Aliev, E. Kunnen, K. Temst, K. Mae, G. Verbanck, J. Barnas, V. V. Moshchalkov, and Y. Bruynseraede, Phys. Rev. Lett. **78**, 134 (1997).
[33]N. L. Schneider, J. T. Lü, M. Brandbyge, and R. Berndt, Phys. Rev. Lett. **109**, 186601 (2012).
[34]K.-S. Li, Y.-M. Chang, S. Agilan, J.-Y. Hong, J.-C. Tai, W.-C. Chiang, K. Fukutani, P. A. Dowben, and M.-T. Lin, Phys. Rev. B **83**, 172404 (2011).
[35]J.-Y. Hong, K.-H. Ou Yang, B.-Y. Wang, K.-S. Li, H.-W. Shiu, C.-H. Chen, Y.-L. Chan, D.-H. Wei, F.-H. Chang, H.-J. Lin *et al.*, Appl. Phys. Lett. **104**, 083301 (2014).
[36]See the supplementary material at http://dx.doi.org/10.1063/1.4903739 for details about: estimation of shot noise, dependence of the conductance with the PTCDA thickness, comparison of the conductance vs. temperature with hopping models, and IETS results.
[37]D. A. Tenne, S. Park, T. U. Kampen, A. Das, R. Scholz, and D. R. T. Zahn, Phys. Rev. B **61**, 14564 (2000).
[38]J. J. H. M. Schoonus, P. G. E. Lumens, W. Wagemans, J. T. Kohlhepp, P. A. Bobbert, H. J. M. Swagten, and B. Koopmans, Phys. Rev. Lett. **103**, 146601 (2009).
[39]Y. Yamauchi, K. Sekiguchi, K. Chida, T. Arakawa, S. Nakamura, K. Kobayashi, T. Ono, T. Fujii, and R. Sakano, Phys. Rev. Lett. **106**, 176601 (2011).
[40]E. Onac, F. Balestro, B. Trauzettel, C. F. J. Lodewijk, and L. P. Kouwenhoven, Phys. Rev. Lett. **96**, 026803 (2006).
[41]Y. Okazaki, S. Sasaki, and K. Muraki, Phys. Rev. B **87**, 041302 (2013).
[42]N. Lambert, R. Aguado, and T. Brandes, Phys. Rev. B **75**, 045340 (2007).
[43]G. Kießlich, E. Schöll, T. Brandes, F. Hohls, and R. J. Haug, Phys. Rev. Lett. **99**, 206602 (2007).
[44]H. Vázquez, R. Oszwaldowski, P. Pou, J. Ortega, R. Pérez, F. Flores, and A. Kahn, EPL **65**, 802 (2004).
[45]S. Yogev, R. Matsubara, M. Nakamura, U. Zschieschang, H. Klauk, and Y. Rosenwaks, Phys. Rev. Lett. **110**, 036803 (2013).
[46]S. Braun, W. R. Salaneck, and M. Fahlman, Adv. Mater. **21**, 1450 (2009).
[47]J. P. Cascales, D. Herranz, F. G. Aliev, T. Szczepański, V. K. Dugaev, J. Barnaś, A. Duluard, M. Hehn, and C. Tiusan, Phys. Rev. Lett. **109**, 066601 (2012).