Spin-filtering transport and switching effect of MnCu single-molecule magnet

H. Hao, X. H. Zheng, Z. X. Dai, and Z. Zeng[a)]
Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China and Graduate School of the Chinese Academy of Sciences, Beijing 100094, People's Republic of China

(Received 12 March 2010; accepted 25 April 2010; published online 13 May 2010)

Electron transport of a single-molecule magnet (SMM) device has been investigated using the first-principles calculations. The SMM based device is constructed by a SMM MnCu [MnCuCl(5-Br-sap)2(MeOH)] bridged between semi-infinite Au(100) electrodes with thiol groups connecting the molecule and the gold electrodes. Our results exhibit crucial features of spin filtering and Kondo resonance. The spin filtering remains robust, whereas the Kondo resonance highly depends on the contact geometry. Specifically, this Kondo resonance can be switched on or off by changing the contact distance. The mechanisms of these features are formulated in details. © *2010 American Institute of Physics*. [doi:10.1063/1.3430063]

During the past few years, it has been demonstrated that the single-molecule magnet (SMM) class[1,2] is attractive to molecular spintronics due to their particular characteristics. Chemically, the rational design and tuning are allowed in SMM-based junctions.[3–8] Physically, SMMs display an impressive array of quantum effects, ranging from quantum tunneling of the magnetization[9,10] to Berry-phase interference[11] and quantum coherence.[12] These quantum effects have important consequence for the physics of spintronic devices. Moreover, the Coulomb-blockade measurement in an individual SMM Mn_{12} shows interesting effects such as negative differential conductance and complete current suppression.[13,14] While the Kondo effect, related to transport through a SMM strongly coupling to metallic electrodes, is predicted based on model Hamiltonian,[15,16] experimentally it remains elusive in SMM-based junctions. The reason may lie in the fact that the core states of SMMs are almost not affected by the leads, thus Bogani and Wernsdorfer[17] proposed that the Kondo resonance might be observable using small SMMs with the core states easily affected by the proximity of electrodes. In this paper, the smallest SMM MnCu (Ref. 18) is used to probe the Kondo effect by first-principles calculations. Our calculations demonstrate the robust spin-filtering effect and the tunable Kondo effect with the change of the contact distance.

We consider the molecular junction with a SMM MnCu bridged between two nanoscale Au(100) electrodes, as shown in Fig. 1. Such nanoelectrodes have been adopted by many authors in the study of molecular devices.[19–21] The magnetic core of the molecule is composed of Mn, Cu, and the coordination atoms (O, N, and Cl). Around the magnetic core are two particular tridentate Schiff base ligands, which establish the strong coupling between the magnetic core and the electrodes. A large enough vacuum layer (with thickness of 20 Å) around the electrode in the x and y direction is chosen so that the device has no interaction with its mirror images. Our calculations are performed by ATK program,[22] in which density-functional theory is combined with the Keldysh nonequilibrium Green's function (NEGF) formalism to calculate the electronic and transport properties of nanoscale systems. The exchange-correlation potential takes the form of the Perdew–Burke–Ernzerhof parametrization of generalized gradient approximation.[23] Only valence electrons are self-consistently calculated and the atomic cores are described by standard norm conserving pseudopotential.[24] The valence wave functions are expanded by localized numerical atomic orbitals,[25] with the single zeta plus polarization basis set for Au atoms and the double zeta plus polarization basis set for other atoms. The Brillouin zone for the electrodes is sampled by a $1\times1\times100$ k-point grid.

In molecular electronics, contact geometries are typical factors that greatly affect transport behaviors of molecular conductors. We therefore examine the effect of the contact distance on the equilibrium conductance of a SMM MnCu.

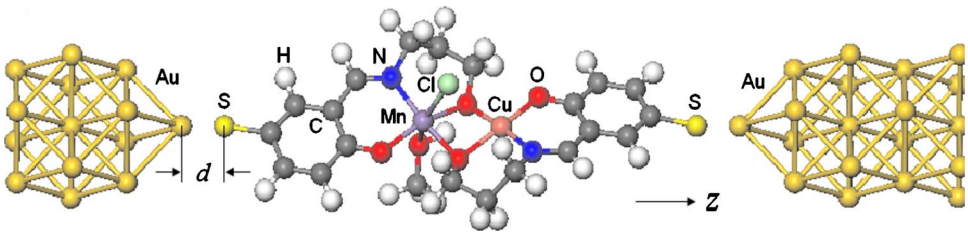

FIG. 1. (Color online) The model structure of the scattering region: MnCu SMM is sandwiched between the two nanoscale Au(100) electrodes. The atom species are identified by color. The two S atoms are used to establish the strong coupling between the molecule and the electrodes. The contact distances are both equally taken as d while z direction is the transport direction.

a)Author to whom correspondence should be addressed. Electronic mail: zzeng@theory.issp.ac.cn.

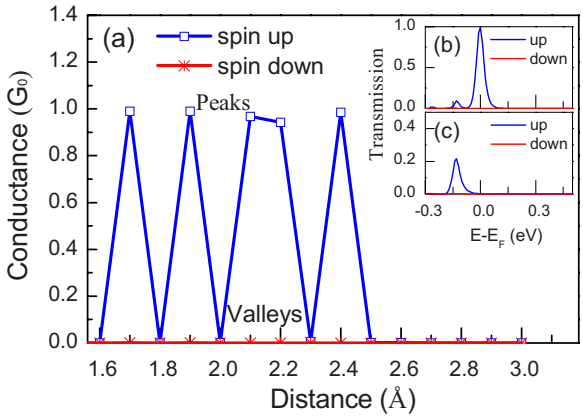

FIG. 2. (Color online) (a) The *G-d* curve: the effect of the contact distance on the Fermi conductance. The inset (b) and (c) show the typical transmission coefficients for peaks and valleys, labeled by Peak and Valley in (a), respectively.

The evolution of the equilibrium conductance with the contact distance is presented in Fig. 2(a). For down spin the equilibrium conductance is almost zero but for up spin strong oscillation is observed in the whole distance region. Here, we take the case of 2.4 Å as an example to examine the spin-filtering effect. As shown in Fig. 3, at the Fermi level electronic states of up spin are almost distributed over the whole system thus a large equilibrium conductance is obtained but for down spin there are hardly any electronic states on certain atoms in the L and R regions. The projected density of states (PDOS) on these atoms gives the quantitative proof of spin-filtering behavior [see Fig. 4(d)]. Therefore, the zero equilibrium conductance for down spin arises from the fact that on certain atoms in the L and R regions no down-spin electronic states can mediate transport. The above understanding is also applicable to other contact distances of 1.7, 1.9, 2.1, and 2.2 Å. However, we should notice that the PDOS on S atoms displays the obvious spin-filtering behavior only in the case of 2.4 Å. Hence a general conclusion could be made that mainly due to the spin-selective coupling between the magnetic atoms and the surrounding organic ligands, the spin-filtering effect is obtained in such system.

More importantly, the equilibrium conductance of up spin exhibits a strong oscillatory behavior as the contact distance varies. Correspondingly, the transmission spectra are reduced to two types for different contact distances. One type is shown in Fig. 2(b) with a peak just being at the Fermi

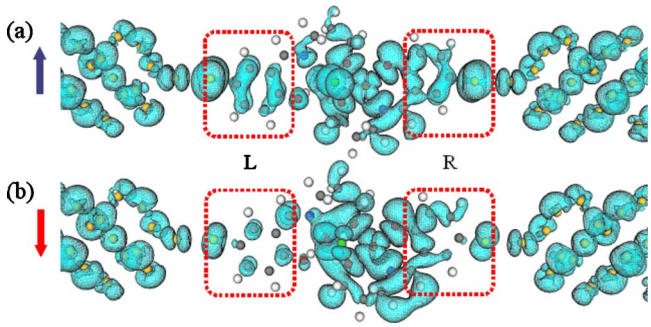

FIG. 3. (Color online) The spatially resolved density of states for up spin and down spin at the Fermi level with the isosurface criterion of 0.02 states/(Å^3 eV) for 2.4 Å: (a) for up spin and (b) for down spin. The "L" and "R" denote the left and the right region, respectively, where a great difference between spin up and spin down is shown.

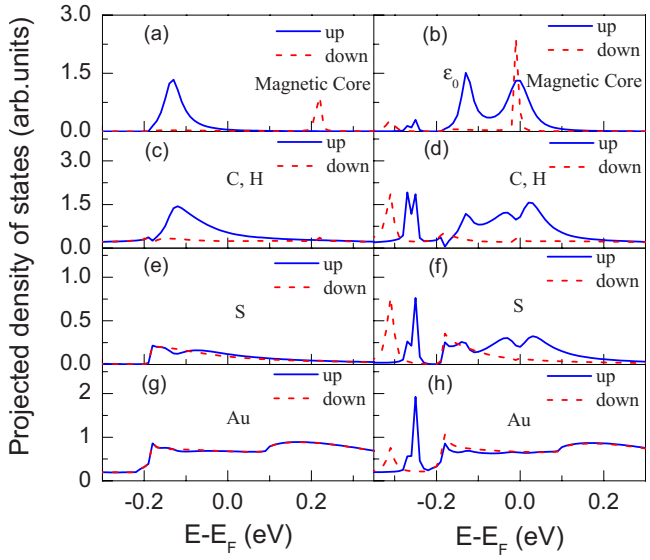

FIG. 4. (Color online) Spin-polarized DOS projected onto certain atoms in the central region: (a), (c), (e), and (g) correspond to the case of 2.0 Å and (b), (d), (f), and (h) correspond to the case of 2.4 Å.

level, and the other is in Fig. 2(c) but with a lower peak below the Fermi level. In the following, this oscillation will be shown to be the switch of Kondo resonance with the change of the contact distance.

One evident feature for this switch of Kondo resonance is that the total magnetic moment (see Fig. 5) of the central molecule also oscillates strongly. It is noteworthy that this oscillation of the magnetic moment is mainly determined by Cu as well as the coordination atoms around it. When the contact distance takes 1.7, 1.9, 2.1, 2.2, or 2.4 Å, the magnetic moment of Cu and its surrounding atoms (N_2, O_2, O_3, and O_4) is almost zero. But for other contact distances, the magnetic moment from these atoms even makes a total difference by nearly 1 μ_B. The above changes on the magnetic moment could also be verified by the spin-polarized molecular projected self-consistent Hamiltonian energy spectrum. It gives total magnetic moment 4 μ_B for 1.7, 1.9, 2.1, 2.2, and 2.4 Å, 3 μ_B for 2.5 and 2.6 Å, and 5 μ_B for 1.6, 1.8, 2.0,

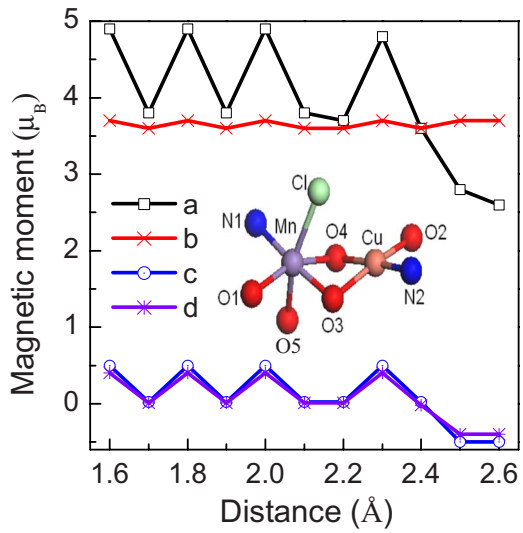

FIG. 5. (Color online) The magnetic moment vs the contact distance: (a) is the total magnetic moment of the molecule, (b) for Mn, (c) for Cu, and (d) for N_2, O_2, O_3, and O_4. The inset is the schematic of the magnetic core.

and 2.3 Å. This oscillating magnetic moment of the molecule could be qualitatively due to the particular tridentate Schiff base ligands, which establish the strong coupling between the magnetic core and the electrodes. The similar oscillations of the conductance and the magnetic moment have been shown in a quantum dot system,[26] which can be switched from a Kondo system to a non-Kondo system as the charge on the dot is changed from odd to even. For SMMs, Romeike *et al.*[15] have shown that for SMMs with half-integer spin ($S>1/2$), the Kondo effect could be observed in zero magnetic field. So for a switch of Kondo resonance it is obvious to obtain 1 μ_B as the minimum change of the magnetic moment. The other notable feature in favor of Kondo resonance is that the PDOS on the magnetic core takes the form of the typical density of states for Kondo resonance [see Fig. 4(b)]. Here ε_0 is the equivalence of the magnetic impurity's energy level in the Anderson model for the Kondo effect and the peak at the Fermi level is exactly the Kondo resonance.[27]

Although in this system the full-integer spin for the Kondo effect is contradictory to that predicted by Romeike *et al.*, we believe that this discrepancy will not influence the Kondo resonance and it could be attributed to the different transverse symmetry of the magnetic anisotropy (TSMA). With the aid of the Berry phase interference this TSMA is very important for spin tunneling in SMMs (Ref. 28) and a special TSMA could make the Kondo effect possible for a SMM with a full-integer spin ($S>1/2$).[29] So we conclude that the switch of Kondo resonance is responsible for the oscillation in the equilibrium conductance with the change of the contact distance.

In summary, we have investigated transport properties through MnCu SMM sandwiched between two nanoscale Au(100) electrodes by first-principles calculations. As the contact distance varies, robust spin-filtering transport properties are obtained due to the spin-selective coupling between the magnetic atoms and the surrounding organic ligands. We have further demonstrated that the oscillating magnetic properties result in the switch of Kondo resonance, which is responsible for the oscillation of the equilibrium conductance.

This work was supported by the National Science Foundation of China under Grant Nos. 10774148, 10904148, and 10804110, the special Funds for Major State Basic Research Project of China (973) under Grant No. 2007CB925004, 863 Project, Knowledge Innovation Program of Chinese Academy of Sciences, and Director Grants of CASHIPS. Part of the calculations was performed in Center for Computational Science of CASHIPS.

[1] G. Christou, D. Gatteschi, D. N. Hendrickson, and R. Sessoli, MRS Bull. **25**, 66 (2000).
[2] D. Gatteschi, R. Sessoli, and J. Villain, *Molecular Nanomagnets* (Oxford University Press, New York, 2007).
[3] A. Cornia, A. F. Costantino, L. Zobbi, A. Caneschi, D. Gatteschi, M. Mannini, and R. Sessoli, Struct. Bonding (Berlin) **122**, 133 (2006).
[4] B. Fleury, L. Catala, V. Huc, C. David, W. Z. Zhong, P. Jegou, L. Baraton, S. Palacin, A. Pierre-Antoine, and T. Mallah, Chem. Commun. (Cambridge) **2005**, 2020 (2005).
[5] A. Naitabdi, J.-P. Bucher, Ph. Gerbier, P. Rabu, and M. Drillon, Adv. Mater. **17**, 1612 (2005).
[6] E. Coronado, A. Forment-Aliaga, A. Gaita-Ariño, C. Giménez-Saiz, F. M. Romero, and W. Wernsdorfer, Angew. Chem., Int. Ed. **43**, 6152 (2004).
[7] L. Bogani, L. Cavigli, M. Gurioli, R. L. Novak, M. Mannini, A. Caneschi, F. Pineider, R. Sessoli, M. Clemente-León, E. Coronado, A. Cornia, and D. Gatteschi, Adv. Mater. **19**, 3906 (2007).
[8] N. Ishikawa, M. Sugita, T. Ishikawa, S.-Y. Koshihara, and Y. Kaizu, J. Phys. Chem. B **19**, 3906 (2007).
[9] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).
[10] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996).
[11] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (1999).
[12] A. Ardavan, O. Rival, John J. L. Morton, and S. J. Blundell, Phys. Rev. Lett. **98**, 057201 (2007).
[13] H. B. Heersche, Z. de Groot, J. A. Folk, and H. S. J. van der Zant, Phys. Rev. Lett. **96**, 206801 (2006).
[14] M. H. Jo, J. E. Grose, K. Baheti, M. M. Deshmukh, J. J. Sokol, E. M. Rumberger, D. N. Hendrickson, J. R. Long, H. Park, and D. C. Ralph, Nano. Lett. **6**, 2014 (2006).
[15] C. Romeike, M. R. Wegewijs, W. Hofstetter, and H. Schoeller, Phys. Rev. Lett. **96**, 196601 (2006).
[16] N. L. Michael and R. M. Eduardo, Phys. Rev. Lett. **97**, 126601 (2006).
[17] L. Bogani and W. Wernsdorfer, Nature Mater. **7**, 179 (2008).
[18] O. Hiroki, N. Masayuki, Y. Ayano, N. Hiroyuki, N. Motohiro, Y. Akira, K. Yoshitomo, and I. Hidehiko, Chem.-Eur. J. **11**, 843 (2005).
[19] J. Taylor, H. Guo, and J. Wang, Phys. Rev. B **63**, 121104 (2001).
[20] B. Larade, J. Taylor, Q. R. Zheng, H. Mehrez, P. Pomorski, and H. Guo, Phys. Rev. B **64**, 195402 (2001).
[21] Z. X. Dai, X. H. Zheng, X. Q. Shi, and Z. Zeng, Phys. Rev. B **72**, 205408 (2005).
[22] M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, Phys. Rev. B **65**, 165401 (2002); J. M. Soler, E. Artacho, J. D. Gale, A. Grcía, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002); J. Taylor, H. Guo, and J. Wang, Phys. Rev. B **63**, 245407 (2001).
[23] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[24] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[25] E. Artacho, D. Sánchez-Portal, P. Ordejón, A. Grcía, and J. M. Soler, Phys. Status Solidi B **215**, 809 (1999).
[26] S. M. Cronenwett, T. H. Oosterkamp, and L. P. Kouwenhoven, Science **281**, 540 (1998).
[27] L. Kouwenhoven and L. Glazman, Phys. World **14** (1), 33 (2001).
[28] M. N. Leuenberger and D. Loss, Phys. Rev. B **63**, 054414 (2001).
[29] G. González, M. N. Leuenberger, and E. R. Mucciolo, Phys. Rev. B **78**, 054445 (2008).