PHYSICAL REVIEW B **88**, 081403(R) (2013)

Thermopower switching by magnetic field: First-principles calculations

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(Received 30 September 2012; published 12 August 2013)

We present first-principles studies of the thermopower of the organometallic V_4Bz_5 molecule attached between Co electrodes with noncollinear magnetization directions. Different regimes in the formation of the noncollinear magnetic state of the molecule lead to a remarkable nonmonotonous dependence of the thermopower on the angle between the magnetizations of the electrodes. This complex behavior is explained by the resonant properties of the electron transmission. Consequently, the nanocontacts can be utilized for local heating or cooling controlled by the external magnetic field.

DOI: 10.1103/PhysRevB.88.081403 PACS number(s): 72.80.−r, 79.10.−n, 85.65.+h, 85.75.−d

The promise of increasing efficiency of energy conversion between thermal and electrical energy makes nanostructures interesting for practical applications. Especially, low-dimensional systems show unusual electrical and thermoelectrical properties as soon as the diameter of these structures decreases towards the nanometer scale.[1–3] The interplay between temperature, electronic structure, and magnetism opened the research field of spin caloritronics[4] investigating spin-dependent thermoelectric properties. Very encouraging results have been obtained for magnetic systems where the spin Seebeck effect[5] or magnetic thermogalvanic voltage[6] are observed. Recent investigations of the thermoelectric properties of tunnel junctions[7] indicate high thermopower and its dependence on the lead magnetization.

In this Rapid Communication we are going further and focusing on the thermoelectric transport properties of a magnetic molecule placed between two macroscopic ferromagnetic leads. We consider the case of leads with different magnetization directions resulting in a noncollinear magnetic structure of the molecule. In particular, we investigate the properties of an organometallic vanadium-benzene V_4Bz_5 ($Bz = C_6H_6$) molecule placed between two magnetic cobalt electrodes in a fcc structure and oriented in the (001) direction (see Fig. 1). These vanadium-benzene complexes have been synthesized and remain stable up to room temperature.[8]

Earlier theoretical investigations of the electronic properties of an infinite vanadium-benzene wire showed that these systems behave like one-dimensional half-metallic ferromagnets.[9] Finite complexes of V_nBz_{n+1} with $n \geqslant 3$ suspended between two Co electrodes with parallel orientation of the lead magnetizations were found to conserve the high spin polarization.[10] The electronic transport properties as well as the magnitude and sign of the thermopower are strongly affected by the number of vanadium-benzene units and by the applied temperature difference.[10]

The present investigation of the electronic transport properties of VBz molecules is based on a combination of *ab initio* density functional theory, as implemented in the SIESTA code[11] with a single particle nonequilibrium Green's function approach realized in the TRANSIESTA code.[12] The latter was extended to systems with noncollinear magnetic order.[13,14] The system under consideration consists of three parts: the left (L) and right (R) semi-infinite Co leads and a central region (C) (Fig. 1). The latter contains the molecule plus parts of the Co electrodes accommodating the molecule surface interaction. The electronic structure calculations were performed using the generalized gradient approximation scheme with Perdew-Burke-Ernzerhof parametrization of the electron exchange-correlation potential.[15] The pseudopotentials for the atomic elements were generated according to the Troullier and Martins procedure[16] with $3p$ semivalent states for the V atom. We use a double-zeta polarized basis set for C, H, and Co atoms and a triple-zeta polarized basis set for V. For the real space grid, we set a uniform mesh corresponding to an energy cutoff of 200 Ry. We found that a 3×3 surface supercell of cobalt is large enough to neglect the interaction between the VBz molecules belonging to different supercells. From the calculations of the total energy of the system we found that the V_4Bz_5 molecule is adsorbed above the hollow site position of fcc Co(001) electrodes. After the adsorption the structure of the first benzene ring next to the surface was deformed and two C-C bonds of the benzene are oriented along the Co(100) direction. Furthermore, we found a small buckling of the Co atoms next to the molecule of about 0.04 Å. The structure of the second benzene ring remains unchanged.

In general, the electron states in a noncollinear magnet cannot be characterized by a certain spin projection on a global quantization axis. Therefore, the wave functions have a spinor structure reflecting a mixture of spin components. The density, potential, and Hamiltonian are 2×2 matrices in spin space.

We use the Landauer formalism for the evaluation of the current,

$$I = \int d\varepsilon\, \tau(\varepsilon)\,[f(\varepsilon - \varepsilon_L, T_L) - f(\varepsilon - \varepsilon_R, T_R)], \qquad (1)$$

where $\varepsilon_{L/R}$ are the Fermi levels of the electrodes, $\tau(\varepsilon)$ is the transmission function,

$$\tau(\varepsilon) = \mathrm{Tr}[\boldsymbol{\Gamma}_L \mathbf{G}_C^+ \boldsymbol{\Gamma}_R \mathbf{G}_C^-], \quad \boldsymbol{\Gamma}_{L/R} = i[\boldsymbol{\Sigma}_{L/R}^+ - \boldsymbol{\Sigma}_{L/R}^-],$$

$f(\varepsilon,T)$ is the Fermi-Dirac distribution function, $\mathbf{G}_C$ is the Green's function of the central region, and $T_{L/R}$ and $\boldsymbol{\Sigma}_{L/R}$ are,

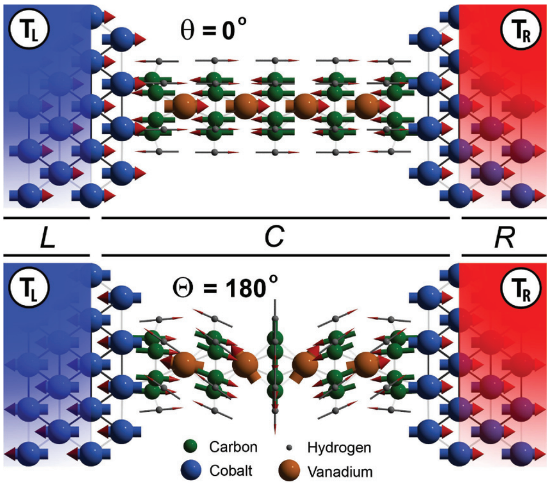

FIG. 1. (Color online) Schematic structure of the V_4Bz_5 nanowire placed between Co(100) electrodes with different magnetization directions. The arrows indicate the direction of the atomic magnetic moments. The electrodes are maintained at different temperatures.

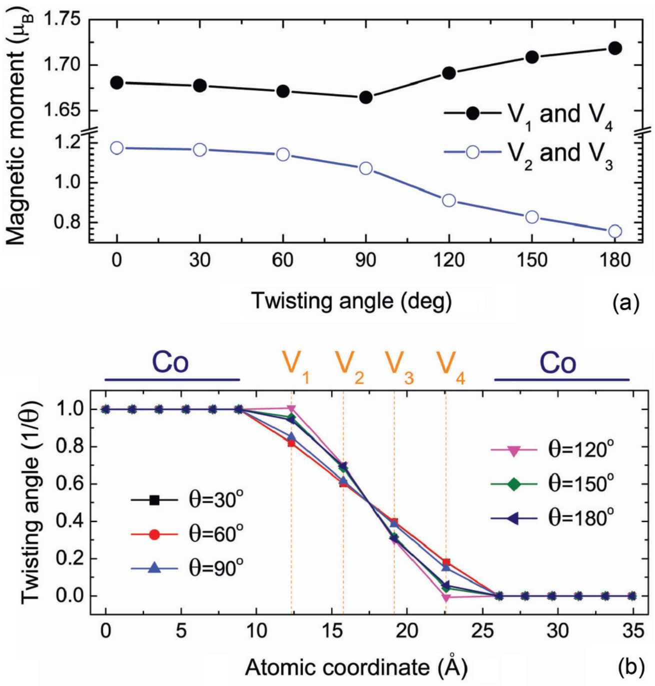

FIG. 2. (Color online) Self-consistently calculated values (a) and directions (b) of the magnetic moments of the V atoms for different twisting angles Θ of the magnetization of the Co electrodes.

respectively, the temperature and self-energy of the left (right) electrode. $\mathbf{G}_C$ and $\mathbf{\Sigma}_{L/R}$ are also 2×2 matrices in spin space.

In the present calculations the angle Θ between lead magnetizations was varied between 0° and 180°. For each Θ the values and directions of the magnetic moments of the central region were relaxed self-consistently. Here we have to note that, for a noncollinear magnetic system, the density, used in the self-consistent procedure, is a complex matrix and therefore one has to use the general relation $\mathbf{D} = i[\mathbf{G}_C^+ + \mathbf{G}_C^-]$, where $\mathbf{G}_C^{+/-}$ are retarded and advanced Green's functions.

For the characterization of thermoelectric transport we evaluate the thermopower S, defined as the ratio of the change in (thermo)voltage with respect to the change in temperature for zero current. To estimate the Seebeck coefficient we use the Landauer formula (1) in combination with the Sommerfeld expansion, leading to

$$S = -\frac{1}{eT}\frac{L_1}{L_0}, \quad L_n = \int_{-\infty}^{\infty}(\varepsilon - \varepsilon_F)^n \tau(\varepsilon)\partial_\varepsilon f(\varepsilon,T)d\varepsilon, \quad (2)$$

where L_n represent the generalized transport coefficients. The integration over energy in the last equation is restricted to an energy window around the Fermi level, since the derivative of the equilibrium distribution function decays fast as a function of energy. The width of the window is determined by the average temperature $T = (T_L + T_R)/2$. For an accurate evaluation of the generalized transport coefficients we use an adaptive method of the energy integration in an interval of $\pm 30 k_B T$ around the Fermi energy ε_F.

In Fig. 2 we present self-consistently calculated values and directions of the spin moments of the V atoms for different twisting angles of the magnetization of the electrodes. Two regimes in the properties of the molecule can be distinguished. For Θ up to 90° the moments of the V_1 and V_4 atoms form with the moments of the corresponding Co electrodes the angle $\sim\Theta/5$ that is close to the angles formed by the moments of the neighboring V atoms in the molecule. On the other hand, for $\Theta > 90°$, the moments of the V_1 and V_4 atoms are almost parallel to the moments of the corresponding leads and the angles between neighboring V spins become close to $\Theta/3$. Also in the values of the V moments there is a change of behavior at 90°: For $\Theta < 90°$, the values of the moments of both inequivalent types of V atoms decrease monotonously and rather weakly. For larger angles the change of the moments with increasing twist becomes considerably faster and opposite for $V_{1/4}$ and $V_{2/3}$ atoms. The presence of the two regimes is important for understanding the unusual thermoelectric properties of the system discussed below.

The thermopower as a function of Θ is presented in Fig. 3. For $T = 60$ K the thermopower is positive for angles $\Theta < 120°$, while for $\Theta > 120°$ it changes sign. The change of the sign is preserved also for higher temperatures. The angular dependence of the Seebeck coefficient changes drastically. The monotonous decrease with increasing Θ obtained for $T =$

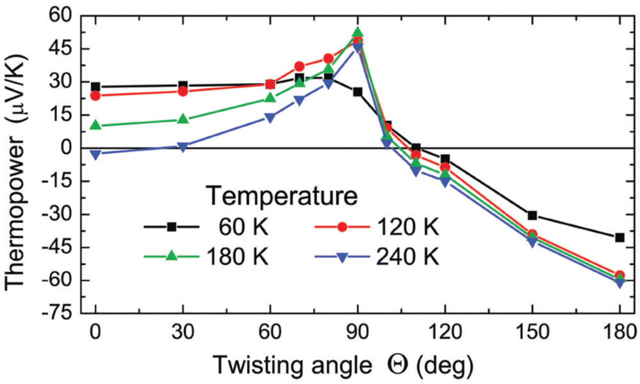

FIG. 3. (Color online) Seebeck coefficient as a function of twisting angles of the lead magnetization Θ for selected temperatures, $T = (T_L + T_R)/2$.

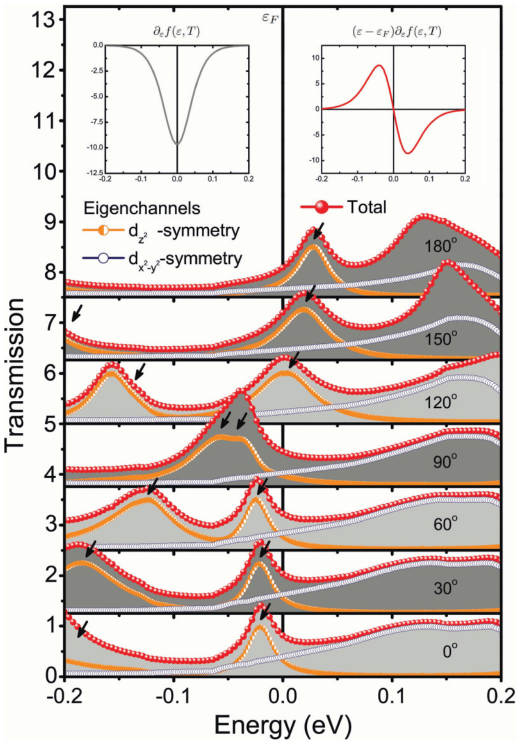

FIG. 4. (Color online) Transmission spectra and the two dominating transmission eigenchannels with d_{z^2} and $d_{x^2-y^2}$ symmetry (z along the molecule) as a function of energy and for different Θ. The insets show the energy dependence of the kernels of the generalized transport coefficients [Eq. (2), $T = 300$ K] for $n = 0$ (left) and $n = 1$ (right). The energy zero is at the Fermi level. Each transmission spectrum is shifted by a constant of 1.25 with respect to the previous one.

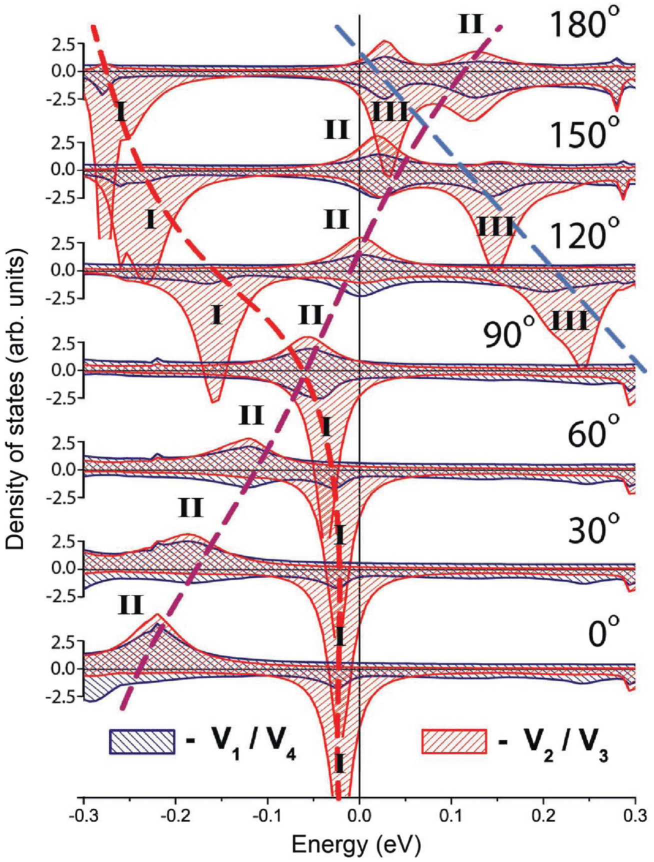

FIG. 5. (Color online) The energy dependence of the spin-polarized density of states of the V$_1$/V$_4$ and V$_2$/V$_3$ atoms with respect to their local magnetization axis for different relative lead magnetization angles Θ.

60 K is replaced with a highly nonmonotonous behavior for larger temperatures. The main changes in the angular dependence are obtained for $\Theta < 90^\circ$ where an almost constant function for $T = 60$ K is replaced by an increasing function with a clear maximum at $\Theta = 90^\circ$. For $\Theta > 90^\circ$ the thermopower decreases monotonously for all temperatures, changing sign at about 120°. Since the change of the twisting angle Θ can be achieved by an external magnetic field, the strong dependence of the thermopower on Θ opens perspectives for device applications of this property. It is worth noting that this effect is similar to the widely applied giant magnetoresistance effect,[17,18] which is a strong dependence of the conductivity on the magnetic configuration of magnetic layers.

To understand the unusual behavior of the thermopower we consider the energy dependence of the electron transmission for different Θ (Fig. 4). It is characterized by a number of resonances whose positions with respect to the Fermi level depend strongly on Θ. The contribution of the resonances to the thermopower is determined by the kernels of the generalized transport coefficients that are shown for the case of $T = 300$ K in the insets in Fig. 4. The derivative of the distribution function $\partial_\varepsilon f(\varepsilon,T)$ is always negative, while the kernel of L_1 changes sign at the Fermi energy. Because of the shape of L_1, the sign of the contribution of a transmission resonance to the thermopower depends on the position of this resonance with respect to ε_F. For all magnetic configurations the calculated transmission exhibits a resonance near the Fermi level. This resonance lies below ε_F for $\Theta < 120^\circ$ and above ε_F for $\Theta > 120^\circ$. Since for low temperatures only the transmission in the nearest neighborhood to ε_F contributes to the thermopower, the crossing of ε_F by the resonance explains the change of the sign of the thermopower with increasing Θ at $T = 60$ K (Fig. 3). At higher temperatures, the electronic states at larger distances from the Fermi level start to play an important role. For example, in the case of parallel lead magnetizations the thermopower changes from 27.8 to -2.5 μV/K (Fig. 3) by changing the temperature from 60 to 240 K. Here, with increasing temperature, the contribution of the states above ε_F increases, leading to the compensation of the contribution of the resonance below ε_F.

To reveal the nature of the transmission resonances we consider the density of states (DOS) of the V atoms for different twisting angles Θ (Fig. 5). In the DOS we can distinguish features related to the crossover between two regimes taking place at $\Theta = 90^\circ$. For angles below 90° the energy region near ε_F is dominated by the peak lying just below ε_F. This peak is responsible for the corresponding transmission resonance (Fig. 5). In the collinear ferromagnetic case ($\Theta = 0^\circ$) the states of this peak are of spin-down character and are localized mostly on the central V atoms (V$_{2/3}$). For noncollinear magnetic structures with $\Theta \neq 0^\circ$ the spin projection is no longer a good quantum number. However, the states of this peak preserve approximately the spin-down character with respect to the local atomic axes. Another important feature of the ferromagnetic DOS is the peak of spin-up states at an energy of about 0.23 eV below ε_F. These states are equally distributed over all V atoms and thus are delocalized over the whole molecule. With increasing Θ these states move towards ε_F, becoming strongly spin mixed, which follows from similar contributions of both spin projections. At $\Theta = 90^\circ$ both peaks of the DOS overlap in the energy region close to and below that of ε_F. These occupied states in the neighborhood of the Fermi level are the origin of the peak in the Seebeck coefficient at $\Theta = 90^\circ$ (Fig. 3).

Above $\Theta = 90^\circ$, peak I, which lies close to ε_F for $\Theta < 90^\circ$, moves quickly to lower energies with a further increase of Θ. Correspondingly, the contribution of this group of states to the Seebeck coefficient decreases quickly. Peak II moves further to higher energies and lies for $\Theta = 180^\circ$ just above ε_F. Simultaneously we observe the movement of a third group of states (III). These are the states of predominantly spin-down character localized mostly on the central V atoms. In contrast to the states of the first peak, they have a d_{xy} character. This group of states appears in the energy interval of interest at $\Theta = 120^\circ$. With a further increase of Θ they move toward ε_F, remaining above it. As a result, at $\Theta = 180^\circ$ there are almost no states just below the Fermi level and many states directly above it. We also found that such strong movement of the electronic states is a result of the strong magnetic interactions between the magnetic centers. The exchange parameters for the nearest neighbors are larger then 66 meV. The effective model and the exchange parameters are shown in Ref. 19.

Based on the properties of the DOS we can understand deeper the properties of the transmission function. In Fig. 4 we show contributions of transmission eigenchannels[20] corresponding to the d_{z^2} and $d_{x^2-y^2}$ states of V. These eigenchannels are closely related to the DOS presented in Fig. 5. The transmission eigenchannel with d_{z^2} symmetry considered for different twisting angles exhibits two resonances, labeled with arrows in Fig. 4. For a twisting angle up to $\Theta = 90^\circ$ one resonance remains at almost an unchanged position just below ε_F whereas the other one moves from below towards the Fermi level. For $\theta > 90^\circ$, the character of the variation of the transmission changes strongly: One of the resonances moves to energies substantially below the Fermi level while the second resonance crosses the Fermi level and lies for larger twisting angles just above ε_F, dominating the transmission. At elevated temperatures the contributions of the $d_{x^2-y^2}$ channel to the transmission is increased, affecting the thermoelectric properties.

The calculations of the transmission spectra for different lengths of the molecule ($n = 3 - 6$) demonstrate the general nature of the dependence of the position and shape of the transmission resonances on the magnetic configuration of the molecule. This effect is seen in Fig. 6 showing the difference in the transmission spectra for parallel and antiparallel lead magnetizations for various n values. However, the important phenomenon of the change of the sign of the thermopower is obtained only for $n = 4$ and $n = 5$ where there is a shift of a resonance from below to above the Fermi level. The quantitative effect is strongest for $n = 4$ where the shift of the resonance through the Fermi level is present most clearly combined with small energy distance of both resonances from the Fermi level. We understand our results as a proof of principle that the sign of the thermopower of the quantum-size device can be manipulated by an external magnetic field. To achieve the desired performance, an optimization of the characteristic of the device is required. First principles calculations provide a very helpful tool for this task.

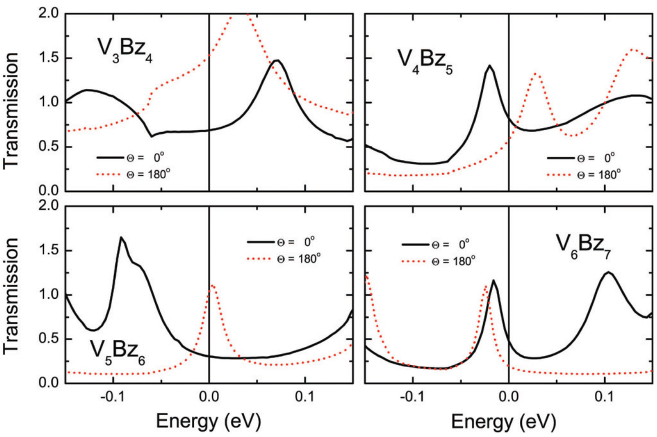

FIG. 6. (Color online) Transmission spectra for parallel ($\Theta = 0^\circ$) and antiparallel ($\Theta = 180^\circ$) lead magnetizations for different lengths of the V$_n$Bz$_{n+1}$ molecule ($n = 3 - 6$).

In summary, our calculations demonstrate that application of an external magnetic field to one of the ferromagnetic electrodes of the Co/V$_4$Bz$_5$/Co system changes the magnetic order and electron transmission, leading to modification of the thermoelectric properties of the system. This results in the magneto-Seebeck effect caused by the temperature gradient that is the analog of the giant magnetoresistance effect caused by an applied bias. In particular, we obtain a sign change of the thermopower as a consequence of the change of the magnetic structure of the organometallic molecule, which implies a potential application as thermoswitch and can be used for local heating or cooling on the nanometer scale controlled by an external magnetic field.

V.V.M thanks I. Maznichenko and A. Bagrets for fruitful discussions. The work was supported by Deutsche Forschungsgemeinschaft via SPP1538 and by the National Academy of Sciences of Ukraine.

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[19] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.88.081403 for the values of the exchange coupling parameters between magnetic centers in the Co-V_4Bz_5-Co system.

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