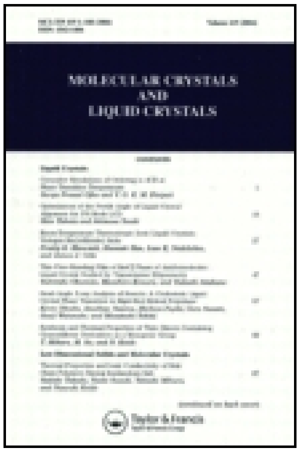

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetic Field Influence on Electron Tunneling through a Molecular Wire

Elmar G. Petrov [a], Igor S. Tolokh [a] & Volkhard May [b]

[a] Bogolyubov Institute for Theoretical Physics, Ukrainian National Academy of Science, 14-b Metrologichna Street, Kiev, 252143, Ukraine

[b] Institut für Physik, Humboldt-Universität zu Berlin, Hausvogteiplatz 5-7, D-10117, Berlin, F. R. Germany

Version of record first published: 04 Oct 2006

Mol. Cryst. Liq. Cryst., Vol. 324, pp. 119–124
Reprints available directly from the publisher
Photocopying permitted by license only

Magnetic Field Influence on Electron Tunneling through a Molecular Wire

ELMAR G. PETROV[a], IGOR S. TOLOKH[a], and VOLKHARD MAY[b]

[a]Bogolyubov Institute for Theoretical Physics, Ukrainian National Academy of Science, 14-b Metrologichna Street, Kiev, 252143, Ukraine; [b]Institut für Physik, Humboldt-Universität zu Berlin, Hausvogteiplatz 5-7, D-10117 Berlin, F. R. Germany

The magnetic field influence on the elastic and inelastic inter-electrode electron tunneling mediated by a molecular wire is studied theoretically. The wire is supposed to include two paramagnetic ions which should be largely separated in space and should reduce their electronic ground-state spin from S to $S - 1/2$ during the formation of an intermediate bound state with the tunneling electron. A field-induced spin polarization of the outgoing low-temperature tunnel current is demonstrated. In the presence of a single-ion anisotropy, a step-like behavior of the current is obtained. Finally, for the inelastic inter-electrode tunneling, a blocking of the tunnel current appears.

Keywords: electron tunneling; magnetic field; molecular wire

1. INTRODUCTION

Electron tunneling (ET) through quasi-one-dimensional molecular structures is thought to be one of the key processes in molecular electronics[1–3]. Embedded between microelectrodes such structures could serve as molecular wires exhibiting different current-voltage characteristics[4–6].

External static and time-dependent fields are among those quantities which should allow to control ET through molecular nanostructures[6,7]. Recently, theoretical studies have been reported on the magnetic field dependence of the elastic inter-electrode ET mediated by a molecular wire[8]. Step-like behavior of the low-temperature tunnel current could be shown for a wire containing a pair of antiferromagnetically coupled paramagnetic ions.

Such a behavior is originated from the (field-independent) quantization of the ion pair spin states and from their field-dependent Zeeman splitting. If the wire contains a single paramagnetic ion, only the field-dependent spin polarization of the outgoing electron tunnel current is observed.

The aim of this paper is to calculate the inter-electrode ET through a molecular wire which contains two largely separated paramagnetic ions. Additionally, the influence of a single-ion anisotropy on the magnetic field dependence of the current should be examined for the low-temperature region. As in[8], each ion is supposed to have a frozen angular momentum and to reduce its electronic ground-state spin from S to $S - 1/2$ if a tunneling electron forms the bound state with the ion. Examples are the ions Mn^{2+} and Fe^{3+} with $S = 5/2$, or Ni^{2+} with $S = 1$.

Two different models of a molecular wire will be analyzed in the following. In the first one we will assume that all bound states formed by the tunneling electron with the wire units are far away from the Fermi levels E_F of the electrodes. In this case the concept of superexchange ET is applicable and an elastic ET goes through the wire. In the second model we provide that the energy levels of the transferred electron at the terminal wire units are positioned near the Fermi levels of the electrodes, and that the relaxation rates within these units largely exceed the ET rates. Now, the terminal wire units can be understood as an intermediate donor (D) and acceptor (A), and an inelastic inter-electrode tunnel current appears.

2. ELASTIC INTER-ELECTRODE TUNNEL CURRENT

Let a voltage V be applied between the left (L) and the right (R) electrodes connected by a molecular wire. Resulting from the effective inter-electrode coupling[4,8], the elastic tunnel current $\mathrm{L} \xrightarrow{J} \mathrm{R}$ can be written (at the presence of an external magnetic field H) as a product of a field-independent (J^0) and a field-dependent part[8]:

$$J = J(H) = J^0 \sum_{\sigma\sigma'} \xi_{\sigma\to\sigma'}(H) . \qquad (1)$$

For the following, we concentrate on the case of two largely separated paramagnetic ions per wire. Using the spin dependence of the intersite electron hopping matrix elements[8], one can derive

$$\xi_{\sigma\to\sigma'}(H) = \sum_{M_1 M_2} \sum_{\overline{M}_1,\overline{M}_2} W_{M_1,M_2}(H) \, |C^{S_2-\frac{1}{2}\,\overline{M}_2+\sigma'}_{S_2\overline{M}_2\,\frac{1}{2}\sigma'} C^{S_1-\frac{1}{2}\,M_1+\sigma}_{S_1 M_1\,\frac{1}{2}\sigma} \times$$

$$\times \sum_{\tilde{\sigma}} C^{S_2-\frac{1}{2}\,M_2+\tilde{\sigma}}_{S_2 M_2\,\frac{1}{2}\tilde{\sigma}} C^{S_1-\frac{1}{2}\,\overline{M}_1+\tilde{\sigma}}_{S_1\overline{M}_1\,\frac{1}{2}\tilde{\sigma}} \delta_{\tilde{\sigma},\sigma+M_1-\overline{M}_1} \delta_{\sigma+M_1+M_2,\sigma'+\overline{M}_1+\overline{M}_2}|^2 , \quad (2)$$

where σ and M_i (σ' and $\overline{M}_i$) are initial (final) spin projections of the tunneling electron and the paramagnetic ions, respectively. The spin-distribution function reads

$$W_{M_1,M_2}(H) = \frac{\exp\left(-E^{mag}_{M_1,M_2}(H)/k_BT\right)}{\sum_{M_1,M_2} \exp\left(-E^{mag}_{M_1,M_2}(H)/k_BT\right)} . \quad (3)$$

It includes the spin-dependent energy of the paramagnetic ions:

$$E^{mag}_{M_1,M_2}(H) = \mu_B g H M_1 + K_1 M_1^2 + \mu_B g H M_2 + K_2 M_2^2 . \quad (4)$$

Here K_i are the single-ion anisotropy constants.

To evaluate the magnetic field effects we introduce the rescaled partial current, $i_{\sigma\sigma'}(H) = \xi_{\sigma\to\sigma'}(H)/\sum_{\sigma\sigma'}\xi_{\sigma\to\sigma'}(H=0, T=0)$; the semipartial current, $i_\sigma(H) = \sum_{\sigma'} i_{\sigma\sigma'}(H)$; and the integral current, $i(H) = \sum_\sigma i_\sigma(H)$.

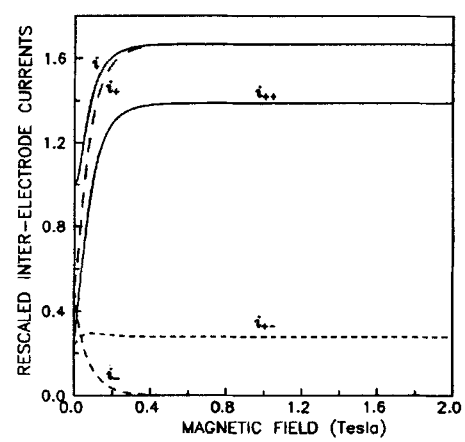

FIGURE 1 The rescaled currents vs magnetic field for the case of elastic ET. $S_1 = S_2 = 5/2$, $k_BT = 1 \times 10^{-5}$ eV, $K_1 = K_2 = 0$.

Figure 1 shows the magnetic field dependence of these currents for the case of an extremely small single-ion anisotropy. As in the case of a single paramagnetic ion per wire[8], the spin-down semipartial current i_- is blocked at $H > 3k_BT/\mu_B g$. Simultaneously, the spin-up current i_+ achieves its maximum and the largest difference in its partial components, i_{++} and i_{+-}. But in contrast to [8], where the integral current does not depend on H, in the present case of two paramagnetic ions, $i(H)$ increases at $H < 3k_BT/\mu_B g$.

Such a behavior is originated from two factors. The first one is given by the blocking of spin-down ET through the paramagnetic ion with the lowest spin projection $M = -S$. Due to the spin reduction ($S' = S - 1/2$) in the bound virtual state of the tunneling electron with the ion as well as the conservation of both the total spin and the total spin projection no ET occurs. The second factor is the spin-flip scattering of the tunneling electron at a paramagnetic ion. If $H > 0$, both factors increase the spin-up probability for the tunneling electron after passing the paramagnetic ion, and they lead to a spin polarization of the outgoing tunnel current.

If the single-ion anisotropy energy largely exceeds k_BT, a competition between the anisotropy energy and the Zeemann energy in (4) leads to a step-like behavior of the current. This is presented in Fig. 2 for the case of

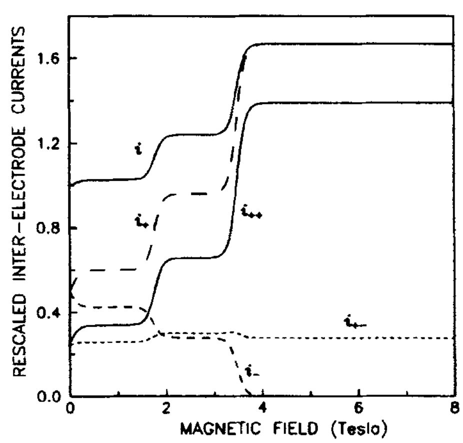

FIGURE 2 The same as in Fig. 1, but for the presence of a single-ion anisotropy. $K_1 = K_2 = 10\,k_BT = 1 \times 10^{-4}$ eV.

two identical ions ($K_1 = K_2 = K$). Each current plateau is characterized by definite ions spin projections such that $M_1 = M_2 = M$ and $W_{M,M}(H) \approx 1$. The number of the plateaus corresponds to the number of possible negative spin projections of the ions. Between neighboring plateaus the transfer occurs if $W_{M,M}(H_{tr}) = W_{M-1,M-1}(H_{tr})$ what results in

$$H_{tr}(M) = K(1 - 2M)/\mu_B g. \tag{5}$$

3. INELASTIC INTER-ELECTRODE TUNNEL CURRENT

In the case of the inelastic ET and in the low-temperature region, the inter-electrode L–R current (L $\xrightarrow{\chi_L}$ D $\xrightarrow{k_1}$ A $\xrightarrow{\chi_{-R}}$ R) depends on the relations between the rate constants k_1, χ_L, and χ_{-R}. If one assumes the D–A ET as the limiting step in the L–R current ($k_1 \ll \chi_L, \chi_{-R}$), one can show that $J \simeq ek_1$. Providing that the superexchange mechanism is valid for the D–A ET (and splitting off the spin independent part k_0 of the rate constant k_1) we obtain

$$J(H) = ek_0 \sum_{\sigma\sigma'} W_{D\sigma}(H)\xi_{\sigma\to\sigma'}(H). \tag{6}$$

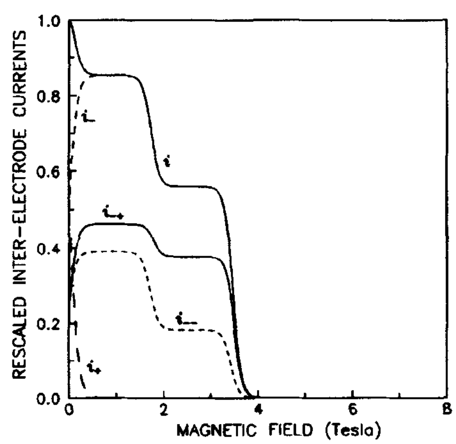

FIGURE 3 Magnetic field dependence of inelastic inter-electrode currents. $S_1 = S_2 = 5/2$, $K_1 = K_2 = 10\,k_BT = 1 \times 10^{-4}$ eV.

$\xi_{\sigma\to\sigma'}(H)$ is defined by (2), and

$$W_{D\sigma}(H) = \frac{\exp(-\mu_B g H\sigma/k_BT)}{\sum_\sigma \exp(-\mu_B g H\sigma/k_BT)} \tag{7}$$

is the distribution function of spin states of the transferred electron being at the D unit (we suppose, the spin-relaxation time $\tau_{sr} \ll \tau_{DA} = 1/k_1$).

The magnetic field dependencies of the rescaled currents are presented in Fig. 3. Similar to the elastic ET, the step-like behavior of the tunnel current occurs as a consequence of the single-ion anisotropy. The magnetic field strengths at which the tunnel current changes from a given plateau to the following are defined by (5). But in contrast to the elastic ET, the spin-up current i_+ decreases rapidly with increasing magnetic field. This behavior results from a lowering of the spin-up state probability (7) which proceeds due to spin relaxation within the D unit. At $H > 3k_BT/\mu_B g$ the integral current is completely defined by i_-. If the magnetic field exceeds $H_{tr}(-S+1)$ and the preferential spin projections of the paramagnetic ions are $M_1{=}M_2{=}-S$ ($W_{-S,-S}(H) \approx 1$), the spin-down current i_- is blocked what results in a complete blocking of the integral tunnel current.

Acknowledgments

The work was supported in part by the Volkswagen-Stiftung, Germany, and by the Fund of Fundamental Researches of the Ukrainian Ministry for Science and Technology, Project No 2.4/625 (E.G.P. and I.S.T.).

References

[1.] C. Joachim and J.P. Launay, *J. Mol. Electron.* **6**, 37 (1990).
[2.] C.M. Fischer, M. Burghard, S. Roth, and K. von Klitzing, *Europhys. Lett.* **28**, 129 (1994).
[3.] *Proceedings of Third European Conference on Molecular Electronics*, edited by F. De Schryver (Catholic Univ. Press, Leuven, 1996).
[4.] V. Mujica, M. Kemp, and M.A. Ratner, *J. Chem. Phys.* **101**, 6849 (1994); **101**, 6856 (1994).
[5.] M. Kemp, A. Roitberg, V. Mujica, T. Wanta, and M.A. Ratner, *J. Phys. Chem.* **100**, 8349 (1996).
[6.] E.G. Petrov, I.S. Tolokh, A.A. Demidenko, and V.V. Gorbach, *Chem. Phys.* **193**, 237 (1995).
[7.] I.A. Goychuk, E.G. Petrov, and V. May, *Chem. Phys. Lett.* **253**, 428 (1996); *J. Chem. Phys.* **106**, 4527 (1997).
[8.] E.G. Petrov, I.S. Tolokh, and V. May, *Phys. Rev. Lett.* **79**, 4006 (1997); *J. Chem. Phys.* **108**, 4386 (1998).