Temperature-dependence of the CISS effect from measurements in Chiral molecular intercalation super-lattices

Subhajit Sarkar
Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva, 84105, Israel and
School of Electrical and Computer Engineering, Ben-Gurion University of the Negev, Beer Sheva, 84105, Israel

Seif Alwan
Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva, 84105, Israel

Amos Sharoni
Department of Physics, Institute of Nanotechnology & Advanced Materials,
Bar-Ilan University, Ramat-Gan, 5290002, Israel

Yonatan Dubi
Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva, 84105, Israel and
Ilse Katz Center for Nanoscale Science and Technology,
Ben-Gurion University of the Negev, Beer Sheva, 84106, Israel

(Dated: November 14, 2022)

We detail here some matters arising from the recent paper by Qin et al., Nature 606, pages 902–908 (2022). We demonstrate, based on data supplied by Qian et al, and corroborated by theoretical modeling, that one of the central conclusions of the manuscript – namely the behavior of the chirality-induced spin-selectivity (CISS) effect at low temperatures – can actually be consistently interpreted in a different way, which is in fact opposite to the interpretation proposed by Qian et al.

In a recent paper Qian, et al., [1] demonstrate chiral molecular intercalation superlattices (CMIS) as a new class of solid-state chiral material platform for exploring chirality induced spin selectivity effect (CISS). Notably, they demonstrate state-of-the-art technique for fabricating well-defined, stable and robust chiral devices with the potential to serve as spintronic devices.

Specifically, Qian et al. show that CMIS can be used to accurately characterize the CISS effect and explore its dependence on temperature, and other material properties. They show a very high degree of polarization of the spin-current $P(T)$, that monotonically decreases with increasing temperature, and the average conductance $G_{SI}(T)$ exhibits an Arrhenius behavior, viz., $G_{SI}(T) = G_0 e^{-\frac{\epsilon_A}{k_B T}}$ corresponding to a thermally activated hopping. The spin-polarized conductance $G_{S}(T)$, on the other hand, exhibits a non-monotonic dependence, increases with temperature at low temperatures up to a certain temperature ($\sim 100$ K) and then decreases. They ascribed this non-monotonic behavior to two mechanisms. The increase up to 100 K is due to electron-phonon interaction assisted increase of the spin-selectivity of the chiral molecule [2, 3], and subsequent decrease is due to the decrease in the electron spin-polarization of the ferromagnetic Cr$_3$Te$_4$ lead.

The origin of the CISS effect is under debate [4] and different theories have been suggested [2,3,6] which show different dependence of the CISS effect on temperature. The interpretation of Qian et.al. [1] is claimed to support the so-called phonon-mechanism for the CISS effect [3].

Here, based on the published data of Qian et.al. [1], we show that the non-monotonicity of the spin-polarized conductance $G_{S}(T)$ may in fact arise from a different mechanism than that proposed by the authors. The low-temperature behavior comes from the Arrhenius envelope of the currents (and not the electron-phonon interaction assisted increase of the spin-selectivity of the chiral molecule), and the reduction at high-temperatures comes from the decrease of magnetism and polarization of the ferromagnetic electrode and from vanishing of the CISS effect at high temperatures. We show that this interpretation is consistent with the experimental findings reported. Based on this we argue that in the CMIS system, the CISS effect actually grows with decreasing temperature.

**TEMPERATURE DEPENDENCE OF THE SPIN-POLARIZED CURRENT**

We start by reiterating the definitions and central result pertaining to the temperature-dependence of the CISS effect of Qian et.al. [1]. The authors measure their CMIS device with two different magnetization directions (parallel and anti-parallel to the direction of current flow), and obtain two currents, marked $I_{\text{high}}$ and $I_{\text{low}}$, the difference between them representing the presence of a CISS effect.

The polarization is defined as $P = \frac{(I_{\text{high}} - I_{\text{low}})}{(I_{\text{high}} + I_{\text{low}})} = \ldots$
I_{S}/I_{tot}$ where $I_{tot}$ is the average current (times 2), and $I_{S}$ is the spin-polarized current. The spin-dependent (or CISS-) conductance is given by $G_{S} = I_{S}/V$. Their central result regarding the CISS effect is that although $G_{S} \to 0$ as $T \to 0$ the $P$ reaches a finite value (60%). This apparent opposite behaviors of $P$ and $G_{S}$ with temperature has been attributed to an increase in the CISS with temperature increase at low temperatures, followed by a global decrease due to the tunneling effect in the material part.

Now, since $P$ and $G_{S}$ are proportional to one another (both having $I_{S}$ in the numerator), the only way this can happen is that if $I_{S}$ and $I_{tot}$ decay to zero as $T \to 0$ with the same functional form. According to Qian, et.al., [1], the average conductance $G_{SI} = I_{high}^{′}(T) + I_{low}^{′}(T)$ exhibits an Arrhenius form with $G_{SI} = G_{0}e^{-\epsilon_A/k_{B}T}$ with an activation energy $\epsilon_A = 12$meV, for a fixed (and of course temperature independent) applied bias $V$ (assuming $V = 0.05$ meV).

Therefore, the individual currents $I_{high}^{′}(T)$ must also exhibit an Arrhenius component when $T \to 0$, i.e., $I_{high}^{′}(T) = I_{low}^{′}(T)e^{-\epsilon_A/k_{B}T}$. This is evident from Fig. ext7(b-e) of Qian et.al., [1], and also supported by the fact that these currents are, after all, charge currents (see discussion in [2]), and therefore they should also be affected by the same mechanism which determines the Arrhenius behavior. Denoting $I_{high}^{′}(T)$ as the Arrhenius normalized charge-current, the spin-conductance must be $G_{SI}(T) = I_{high}^{′}(T) - I_{low}^{′}(T)e^{-\epsilon_A/k_{B}T} = \Delta I^{′}(T)e^{-\epsilon_A/k_{B}T}$. This implies that the vanishing of $G_{S}$ with decreasing temperature comes from the Arrhenius part, and the part coming from the CISS effect is actually $\Delta I^{′}(T)$, the “Arrhenius normalized” spin-polarized current.

To show this from the data, we digitally extract the temperature dependence of individual charge currents from Figs. 5a and ext7a of Qian et.al. [1]. Fig. 1(a) shows the “Arrhenius normalized” currents, $I_{high}^{′}(T)$, as a function of temperature $T$. $I_{high}^{′}(T)$ decreases monotonically with increasing temperature, while $I_{low}^{′}(T)$ first decreases and then increases, indicating non-monotonicity. However, Fig. 1(b) shows that their difference $\Delta I^{′}(T)$ decreases monotonically with increasing temperature, clearly indicating a monotonic decrease in the CISS effect.

Therefore, a consistent interpretation of the data (pointing again that the polarization $P$ and the CISS conductance $G_{S}$ show distinctly different behaviors as $T \to 0$) is that the CISS effect is finite at low temperatures and vanishes with increasing temperature, while the total charge current increases with temperature, after being nearly zero at low temperatures. The competition between these two processes leads to non-monotonicity in $G_{S}$ but to a monotonic polarization $P$.

Qian et.al. [1] Interpreted their data using the Jullier model [3], which implies $G_{S} = G_{P}P_{1}P_{2}$, where $P_{1}$ and $P_{2}$ are polarization of the Ferromagnetic lead and the equivalent polarization of the chiral molecular layers, respectively, and $G_{P}$ is the overall conductance envelope. Following the convention in their paper, the spin conductance can be directly expressed as $G_{S} = G_{SI}P$, where $P$ is related to the polarizations of the two layers and $G_{T}$ to $G_{SI}$. The authors suggest, based on previous studies of different systems [3] (Ref. 50 in Qian, et.al., [1]) that $G_{P}$ is temperature-independent. However, in their system, $G_{T}$ seems to be strongly temperature-dependent, and has an Arrhenius form which vanishes at low temperatures based on our picture.

Thus, the data provided by Qian, et.al., [1] can be interpreted by a mechanism for the CISS effect in which the CISS effect is enhanced when the temperature is reduced, such as the mechanism proposed by Alwan and Dubi [4]. To further corroborate this claim, we performed a calculation based on the theory of Ref. [9], modified to account for the specific Arrhenius-type I-V characteristics observed in the experiments performed by Qian.
FIG. 2. (a) Calculated polarization (in %), (b) current (in nA) and (c) spin conductance (in nS) as functions of temperature (K), based on the theoretical approach of Ref. [3]. The respective insets depict the experimental data points, extracted from Qian, et.al., [1]. A qualitative resemblance between theory and data is clearly visible.

et.al., [1] (see Supplementary Information for calculation details). The results of the calculation are presented in Fig. 2 showing the polarization $P$ (Fig. 2(a)), the high and low currents (Fig. 2(b)) and the spin conductance $G_s$ (Fig. 2(c)), all as a function of temperature. The insets show the experimental data. The qualitative resemblance between the theory and the data is clearly visible.

In conclusion, Qian, et.al., [1] demonstrate that they are able to fabricate a remarkable, robust solid-state chiral material platform, based on chiral molecules intercalated between two-dimensional atomic crystals, which exhibits the CISS effect. However, a consistent analysis of their data may imply that, in opposite to their suggestion, the CISS effect is finite at low temperatures and is reduced with increasing temperature. Thus, their data is more consistent with other suggestions for the origin of the CISS effect (e.g. the “spinterface” model suggested by Alwan and Dubi [5, 6]) than with the phonon mechanism for the CISS effect [3]. We therefore encourage the authors to use these remarkable device to continue and study the CISS effect, e.g. by going to even lower temperatures or by changing the electrode material. Such measurements with high quality data (as provided by Qian et al.) are necessary to help the community to fully understand the origin of the CISS effect.

Appendix A: Calculations Details

In the limit of weak coupling, compared to the temperature, between the molecular level and the electrodes, one can resort to the formulation of rate equations that simplifies the expressions for currents [5]. For simplicity, we consider a single molecular level that mimics the complicated transport set-up fabricated in Ref. [1]. We treat the transport set-up corresponding to Ref. [1] as a single level with an effective LUMO equal to the thermal activation energy. This way, we can separate the true thermal effects (i.e., the Arrhenius dependence found in Ref. [1]) from the spin-dependent effects.

The expression for currents are given by [5],

$$I_{\sigma} = \frac{\gamma_L \gamma_{R\sigma}}{\gamma_L + \gamma_{R\sigma}} [f_{L\sigma}(\epsilon_0, V) - f_{R\sigma}(\epsilon_0, V)],$$  \hspace{1cm} (A1)

where $f_{X\sigma}(\epsilon_A, V) = \left[ 1 + e^{\beta(\epsilon_0 - \mu_{X\sigma} \pm V/2)} \right]$ corresponds to the Fermi-Dirac distribution of the left ($X=L$) and right ($X=R$) electrodes with spin dependent chemical potential $\mu_{\sigma} = \sigma \alpha_A \cos \theta$, $\alpha_A$ being the maximal effective Zeeman coupling in the Au electrode, and $\sigma = \pm1$ for spin-up and -down, respectively (up and down are now defined in the $z$-direction). Here, $\gamma_L$ and $\gamma_R$ are the tunneling rates between the L and R-electrode and the molecular level, respectively, and $\alpha_A$ is the spin-orbit coupling (SOC) strength of the metallic electrode, and $\theta$ is the angle between the surface magnetization in the metallic electrode and the principle axis of the molecules.

We simplify the expression of the current in (A1) as

$$I_{\text{low(high)}} = \frac{\gamma_L}{2} e^{-\beta \epsilon_A} e^{[\pm \beta \alpha_A \cos \theta]}$$  \hspace{1cm} (A2)

for spin-down (low) and spin-up (high) electrons, respectively. In this simplification we have assumed that $\gamma_L = \gamma_{R\sigma} = \gamma$ and $\epsilon_0 = \epsilon_A$, i.e., LUMO of the single level is equivalent (and equal) to the thermal activation. The total current and spin-polarization are given by $I = I_{\text{high}} + I_{\text{low}}$ and $IS = I_{\text{high}} - I_{\text{low}}$, respectively.

Similarly, the densities of spin-up (-down) electrons are given by,

$$n_{\sigma} = \frac{1}{2} \left[ f(-\sigma \alpha_A \cos \theta + V/2 + \epsilon_0) + f(-\sigma \alpha_A \cos \theta - V/2 + \epsilon_0) \right].$$  \hspace{1cm} (A3)

We linearize (A3) around $(V, \beta, \epsilon_0 = \epsilon_A, \alpha_A) = (0, 0, 0, 0)$ and find the spin-polarization $\Delta S = n_+ - n_- = \frac{1}{2} \beta \alpha_A \cos \theta$. 

We linearize (A3) around $(V, \beta, \epsilon_0 = \epsilon_A, \alpha_A) = (0, 0, 0, 0)$ and find the spin-polarization $\Delta S = n_+ - n_- = \frac{1}{2} \beta \alpha_A \cos \theta$. 

$$\Delta S = \frac{1}{2} \beta \alpha_A \cos \theta.$$  \hspace{1cm} (A4)
The spin-interface mechanism provides a finite value of the otherwise random angle $\theta$ [5]. In a non-chiral molecule, $\langle \cos \theta \rangle = 0$, therefore, no spin filtering. The spin-interface mechanism states that as current passes through the junction, the chiral motion of electrons induces a small solenoid magnetic field in the direction of the molecule. This field is then felt by the (angular momentum) magnetic moment of the interface Au orbitals, as a feedback effect from the (tiny) spin-polarized current, stabilizing the angle to $\langle \cos \theta \rangle = \cos \theta_M$. This average angle $\theta_M$ is determined self consistently via the equation, $\cos(\theta_M) = B(\alpha_0 I + \alpha_1 \frac{1}{2} \beta \alpha_A \cos \theta_M)$, where $B(x) = \frac{J_1(x)}{J_0(x)}$. Here $J_n$ are the Bessel functions of the first kind, $\alpha_0$ is the strength of the solenoidal field, and $\alpha_1$ relates to the strength of the spin transfer torque. Then the currents and spin-polarization are calculated using, $I_{\text{low(high)}} = \gamma e^{-\beta \epsilon} A e^{[\pm \beta \alpha_A \cos \theta_M]}$ and $\Delta S = \frac{1}{2} \beta \alpha_A \cos \theta_M$, respectively.

[1] Q. Qian, H. Ren, J. Zhou, Z. Wan, J. Zhou, X. Yan, J. Cai, P. Wang, B. Li, Z. Sofer, et al., Chiral molecular intercalation superlattices, Nature 606, 902 (2022).
[2] T. K. Das, F. Tassinari, R. Naaman, and J. Fransson, Temperature-dependent chiral-induced spin selectivity effect: Experiments and theory, The Journal of Physical Chemistry C 126, 3257 (2022).
[3] J. Fransson, Vibrational origin of exchange splitting and chiral-induced spin selectivity, Physical Review B 102, 235416 (2020).
[4] F. Evers, R. Korytár, S. Tewari, and J. M. van Ruitenbeek, Advances and challenges in single-molecule electron transport, Rev. Mod. Phys. 92, 035001 (2020).
[5] S. Alwan and Y. Dubi, Spinterface origin for the chirality-induced spin-selectivity effect, Journal of the American Chemical Society 143, 14235 (2021).
[6] Y. Dubi, Spinterface chirality-induced spin selectivity effect in bio-molecules, Chemical Science 10.1039/D2SC02565E (2022).
[7] J. Fransson, The chiral induced spin selectivity effect—what it is, what it is not, and why it matters, arXiv preprint arXiv:2202.02512 (2022).
[8] M. Julliere, Tunneling between ferromagnetic films, Physics letters A 54, 225 (1975).
[9] C. H. Shang, J. Nowak, R. Jansen, and J. S. Moodera, Temperature dependence of magnetoresistance and surface magnetization in ferromagnetic tunnel junctions, Physical Review B 58, R2917 (1998).