



# CHORUS

This is the accepted manuscript made available via CHORUS. The article has been published as:

## Magnetization Control and Transfer of Spin-Polarized Cooper Pairs into a Half-Metal Manganite

A. Srivastava, L. A. B. Olde Olthof, A. Di Bernardo, S. Komori, M. Amado, C. Palomares-Garcia, M. Alidoust, K. Halterman, M. G. Blamire, and J. W. A. Robinson

Phys. Rev. Applied **8**, 044008 — Published 17 October 2017

DOI: [10.1103/PhysRevApplied.8.044008](https://doi.org/10.1103/PhysRevApplied.8.044008)

# Magnetization-control and transfer of spin-polarized Cooper pairs into a half-metal manganite

A. Srivastava<sup>1</sup>, L. A. B. Olde Olthof<sup>1,2</sup>, A. Di Bernardo<sup>1</sup>, S. Komori<sup>1</sup>, M. Amado<sup>1</sup>, C. Palomares-Garcia<sup>1</sup>, M. Alidoust<sup>3</sup>, K. Halterman<sup>4</sup>, M. G. Blamire<sup>1</sup>, and J. W. A. Robinson<sup>1\*</sup>

<sup>1</sup>*Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom*

<sup>2</sup>*Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands*

<sup>3</sup>*Department of Physics, K.N. Toosi University of Technology, Tehran 15875-4416, Iran*

<sup>4</sup>*Michelson Lab, Physics Division, Naval Air Warfare Center, China Lake, California 93555, USA*

The pairing state and critical temperature ( $T_C$ ) of a thin  $s$ -wave superconductor ( $S$ ) on two or more ferromagnets ( $F$ ) are controllable through the magnetization-alignment of the  $F$  layers. Magnetization misalignment can lead to spin-polarized triplet pair creation, and since such triplets are compatible with spin-polarized materials they are able to pass deeply into the  $F$  layers and so, cause a decrease in  $T_C$ . Various experiments on  $S/F_1/F_2$  “triplet spin-valves” have been performed with the most pronounced suppression of  $T_C$  reported in devices containing the half-metal ferromagnet (HMF)  $\text{CrO}_2$  ( $F_2$ ) albeit using out-of-plane magnetic fields to tune magnetic non-collinearity [Singh *et al.*, Phys. Rev. X 5, 021019 (2015)]. Routine transfer of spin-polarized triplets to HMFs is a major goal for superconducting spintronics so as to maximize triplet-state spin-polarization. However,  $\text{CrO}_2$  is chemically unstable and out-of-plane fields are undesirable for superconductivity. Here, we demonstrate low field (3.3 mT) magnetization-tuneable pair conversion and transfer of spin-polarized triplet pairs to the chemically stable mixed valence manganite  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  in a pseudo spin-valve device using in-plane magnetic fields. The results match microscopic theory and offer full control over the pairing state.

PACS numbers: 74.78.Na, 74.20.-z, 74.25.Ha

## I. INTRODUCTION

Superconducting spintronics represents a new paradigm for information processing involving the coexistence of spin-polarization and superconducting phase coherence [1–3]. Conventional  $s$ -wave superconductivity involves the condensation of spin-singlet electron pairs with antiparallel spins. Although singlet pairs are energetically unstable in a ferromagnet, they are able to penetrate a transition metal ferromagnet ( $F$ ) at a superconductor/ferromagnet ( $S/F$ ) interface over distances of a few nanometers [4–10], but without transferring a net spin. Furthermore, singlet pairs are blocked at a  $S$  interface with a half metallic ferromagnet (HMF) as there are no available states for one of the two spins of a pair to enter since the Fermi energy for the minority-spin electrons falls within a gap.

Electrons pairs in the  $p$ -wave superconducting compound  $\text{Sr}_2\text{RuO}_4$  [11] have parallel spins and so such spin-triplet pairs carry a net spin in addition to charge. However, the extreme sensitivity of  $p$ -wave superconductivity to structural and electronic disorder, creates major obstacles to the development of  $p$ -wave devices [12]. Spin-triplet pairs with parallel spins, but  $s$ -wave symmetry may form at magnetically inhomogeneous  $s$ -wave  $S/F$  interfaces [1–3]. Since such pairs are compatible with fully spin-polarized materials, their routine creation and transfer to HMFs would open up exciting opportunities for applications in superconducting spintronics where high spin-polarization and long spin-flip scatter lengths are desirable.

---

\* [jjr33@cam.ac.uk](mailto:jjr33@cam.ac.uk)

49 Spin-polarized triplet pairs form via spin mixing and spin-rotation processes at  $S/F$  interfaces [13]. At  
50 homogeneously magnetized  $S/F$  interfaces or within magnetically collinear  $S/F_1/F_2$  spin-valves, spin-  
51 singlet pairs experience a spatially constant exchange field that acts differentially on the antiparallel  
52 spins of a pair, causing transformation to a spin-zero triplet state (spin-mixed state). A rotation of the  
53 magnetization at a  $S/F$  interface or within a  $S/F_1/F_2$  spin-valve has the effect of transforming spin-  
54 zero triplets to pairs with a parallel projection of spin (spin-rotation). For  $S/F_1/F_2$  spin-valves where  $S$   
55 and  $F_1$  ("spin-mixer" layer) are thinner than the spin-singlet coherence length (40 nm in Nb [14] and 1  
56 nm in Co, Fe and Ni [15, 16]), spin-polarized triplet pair creation leads to an effective leakage of  
57 superconductivity from  $S$  into  $F_2$  and a reduction of the critical temperature ( $T_C$ ). "Triplet spin-valves"  
58 (TSVs) are therefore sensitive devices for investigating singlet-to-triplet pair conversion [17–20].  
59

60 Experiments over the past few years have mainly focused on magnetization-control of triplet pair  
61 creation in  $S/F/S$  Josephson devices and TSVs. In  $S/F/S$  devices various symmetric spin-mixer layers  
62 have been added to the  $S/F$  interfaces, including rare earth magnetic spirals [21, 22],  
63 antiferromagnets [23], Heusler alloys [24], and transition metal ferromagnets [25–29]. Similarly in  
64  $S/F_1/F_2$  TSVs,  $F_{1,2}$  metals [30–33] or  $F$  metals ( $F_1$ ) in combination with the HMF  $\text{CrO}_2$  ( $F_2$ ) [34] have  
65 been successfully demonstrated. See also related works on  $F/S/F$  spin-valves [35–37] and  
66 spectroscopy experiments on various  $S/F$  systems experiments [38–48].  
67

68 The most pronounced suppressions of  $T_C$  was reported in a  $\text{MoGe}/\text{Ni}/\text{Cu}/\text{CrO}_2$  TSV in which out-of-  
69 plane magnetic fields created a misalignment between the magnetizations of Ni and  $\text{CrO}_2$  [34]; the  
70 largest suppression of  $T_C$  was close to -800 mK with a constant out-of-plane magnetic field of 2 T. This  
71 pioneering work extended previous experiments that demonstrated Josephson coupling across  $\text{CrO}_2$   
72 [49] (see also [27,35]) in devices that did not contain intentional spin-mixer layers at the  $S/\text{HMF}$   
73 interfaces. However,  $\text{CrO}_2$  is chemically unstable and so there is a need to identify alternative HMFs  
74 in which thin films can be grown and combined with various  $S/F$  structures with enhanced chemical  
75 stability.  
76

77 Mixed valance manganites ( $\text{La}_{1-x}\text{Ae}_x\text{MnO}_3$ , where Ae is an alkaline earth) such as  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  (LSMO)  
78 and  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LCMO) are highly attractive alternatives to  $\text{CrO}_2$  since they are chemically stable  
79 and their relatively narrow spin up and spin down conduction bands are completely separated leading  
80 to HMF behaviour at low temperatures[50, 51]. In this *Article*, we report TSV with  
81  $\text{Nb}/\text{Cu}/\text{Py}/\text{Au}/\text{LCMO}$  layers in which a non-monotonic dependence of  $T_C$  on the relative magnetization  
82 angle ( $\theta$ ) between  $\text{Py}(\text{NiFe})$  and LCMO is observed, thus demonstrating pair conversion and transfer  
83 of spin-polarized triplets to LCMO. Recently, we detected Josephson coupling across thin ( $< 30$  nm)  
84 layers of LCMO [52], but without intentional spin-mixers at the  $S/\text{LCMO}$  interfaces. Related  
85 experiments that probe spectroscopic signatures triplet pairing in  $S/\text{LCMO}$  structures have also been  
86 reported [42–44, 53], but again without intentional spin-mixer layers. The motivation of the work  
87 reported here was to investigate magnetization-control of triplet pair creation and transfer to LCMO,  
88 which is fundamental to the development triplet superconductivity based on mixed valance  
89 manganites. Furthermore, we wanted to demonstrate triplet pair creation in TSVs with small in-plane  
90 magnetic fields to avoid complications due vortices that will be present in TSV that require large out-  
91 of-plane magnetic fields  
92

## 93 II. EXPERIMENT

94  
95 We prepared  $\text{Nb}(25\text{nm})/\text{Cu}(5\text{nm})/\text{Py}(3.5\text{nm})/\text{Au}(5\text{nm})/\text{LCMO}(120\text{nm})$  TSVs in several stages. Epitaxial  
96 (002) LCMO was grown from a stoichiometric target by pulse laser deposition (PLD) (KrF laser,  
97 wavelength  $\lambda = 248$  nm) on 5 mm x 5mm single crystal  $\text{SrTiO}_3$  (001) at a growth temperature of 800 °C  
98 in flowing  $\text{N}_2\text{O}$  at 130 mTorr with a pulse fluence of  $1.5 \text{ J}/\text{cm}^2$  for 15 minutes and repetition rate of 2  
99 Hz, then 30 minutes at 3 Hz. The films were annealed *in situ* at the same temperature in oxygen (46  
100 kPa) for 8 hours and cooled to room temperature at a rate of 10 °C/min. High resolution X-ray

101 diffraction (Fig. 1S) confirmed single (002) orientation of LCMO with rocking curves on the (002),  
102 (004), (006) and (008) Bragg peaks showing full width at half maximum values of 0.12°, 0.18°, 0.209°  
103 and 0.227°, respectively. The c-axis lattice parameter was determined to be 7.670±0.002 Å, consistent  
104 with powder diffraction simulations [54]. Au was deposited on LCMO at room temperature using a  
105 fluence of 2.5 J/cm<sup>2</sup> for 3 minutes at 5 Hz in 30 mTorr of Ar (Au was chosen due to its oxidation  
106 resistance and limited solubility with Ni). Au/LCMO bilayers were then transferred in air to an  
107 ultrahigh vacuum sputtering system with a base pressure of 3 × 10<sup>-9</sup> mBar and Nb/Cu/Py trilayers  
108 were deposited on Au/LCMO in Ar at 1.5 Pa while rotating below stationary magnetrons. The surface  
109 of Au was cleaned in situ by Ar ion plasma etching (-0.6 kV extraction energy and 1 kV ion energy) and  
110 different etching times in the 0-5 minute range were investigated. During the sputter process,  
111 samples experienced a constant in plane magnetic field of approximately 50 mT.

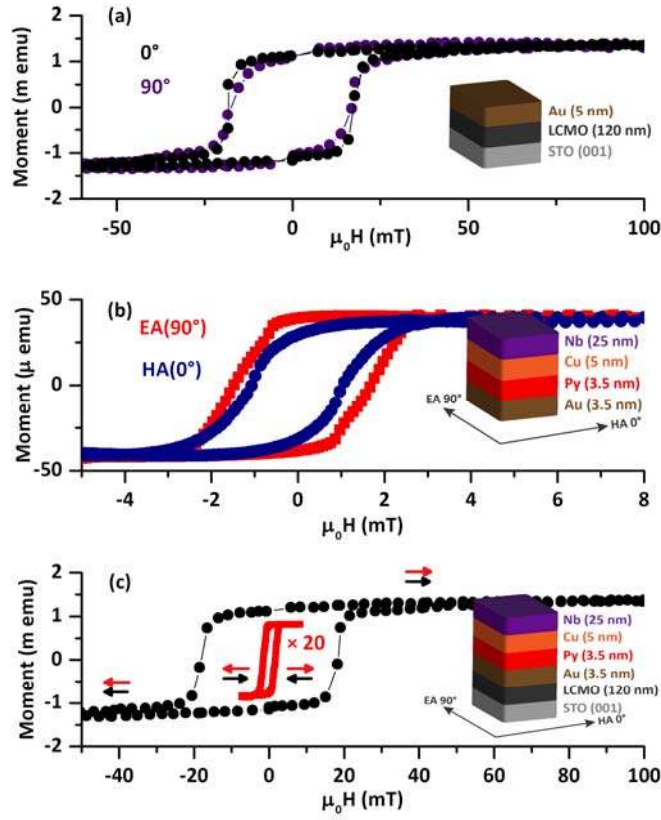
112  
113 Control samples of Au(5nm)/LCMO(120nm) and Nb(25nm)/Cu(5nm)/Py(3.5nm)/Au(5nm) were  
114 prepared on 5 mm x 5 mm area STO (001) and single crystal silicon substrates, respectively, to  
115 characterize the isolated magnetic properties of LCMO and Py. Magnetization  $M$  versus applied field  
116  $H$  is shown in Fig. 1(a,b) at 10 K. The  $M(H)$  of LCMO shows an easy-plane behaviour with an in-plane  
117 saturation field ( $H_s$ ) of 50 mT and coercivity ( $H_c$ ) of 20 mT. In the Supplemental Materials [55] we also  
118 show that (Fig. 4S) the LCMO is magnetically isotropic in-plane at 10 K. In comparison, the Py shows  
119 some in plane anisotropy with an easy axis (EA, defined as 90°) parallel to the field direction during  
120 growth and  $H_c$  of 1.8 mT and a harder axis (HA, defined as 0°) at a right angle to the EA with  $H_c = 1.1$   
121 mT. The volume saturation magnetizations of LCMO and Py were 470±15 emu/cm<sup>3</sup> and 650±25  
122 emu/cm<sup>3</sup> respectively, which are similar to values reported elsewhere [For LCMO see [56] and [57] for  
123 Py].

124  
125 Figure 1(c) shows  $M(H)$  of the TSV at 10 K where  $M$  is dominated by the 120-nm-thick LCMO layer and  
126 so, for comparison easy-axis  $M(H)$  loop is plotted for the Nb/Cu/Py/Au control (reproduced from Fig.  
127 1(b)). The  $M(H)$  loops show that the TSV magnetization state is parallel (P) beyond ±30 mT, and a  
128 reversal field of -1.8 mT switches the Py moment to achieve an antiparallel (AP) state.

129  
130 Resistance vs temperature  $R(T)$  measurements of the TSVs were performed using a four-point  
131 current-bias technique on unpatterned samples in a pulse-tube measurement system. The  $T_c$  was  
132 defined as the temperature corresponding to 50% of the normal state resistance. We note that care  
133 was taken to ensure that the bias-current (10 μA) had no effect on  $R(T)$  through the superconducting  
134 transition and therefore that the  $T_c$  was current-bias independent (meaning the bias-current is not  
135 large enough for vortex-induced voltages to dominate the transport signal). In all cases,  $R(T)$  did not  
136 show anomalies (e.g. steps) through the superconducting transition.

137  
138 The effect of in-plane magnetization configuration on  $T_c$  was investigated by measuring  $R(T)$  though  
139 the superconducting transition as a function of the relative magnetization angle ( $\theta$ ) between LCMO  
140 and Py. The  $T_c(\theta)$  measurement routine is illustrated in Fig. 2(a) and described here: (1) at 10 K an  
141 external field of 100 mT was applied along the HA of Py to magnetize LCMO and Py (along 0°); (2) a  
142 magnetic field of -3.3 mT ( $<H_c$  of LCMO) was then applied along the HA of Py to reverse the Py  
143 moment and obtain the AP-state (along 180°) and from  $R(T)$  in cooling and warming  $T_c(180^\circ)$  was  
144 obtained; (3) the sample warmed to 10 K and rotated in-plane to an angle  $\theta$  in a constant field of  
145 amplitude 3.3 mT and from  $R(T)$  in cooling and warming  $T_c(\theta)$  was obtained. Stage (3) was repeated  
146 at 20° increments to obtain  $T_c(\theta)$  between 0° - 180°. We note that a field of -3.3 mT was large enough  
147 to fully magnetize Py in all in-plane field directions without altering the remnant state of LCMO.

150  
151  
152  
153  
154  
155  
156  
157  
158  
159  
160  
161  
162  
163  
164  
165  
166  
167  
168  
169  
170  
171  
172  
173  
174  
175  
176  
177  
178  
179  
180  
181  
182  
183  
184  
185  
186  
187  
188  
189  
190  
191  
192  
193  
194  
195  
196  
197  
198  
199  
200  
201



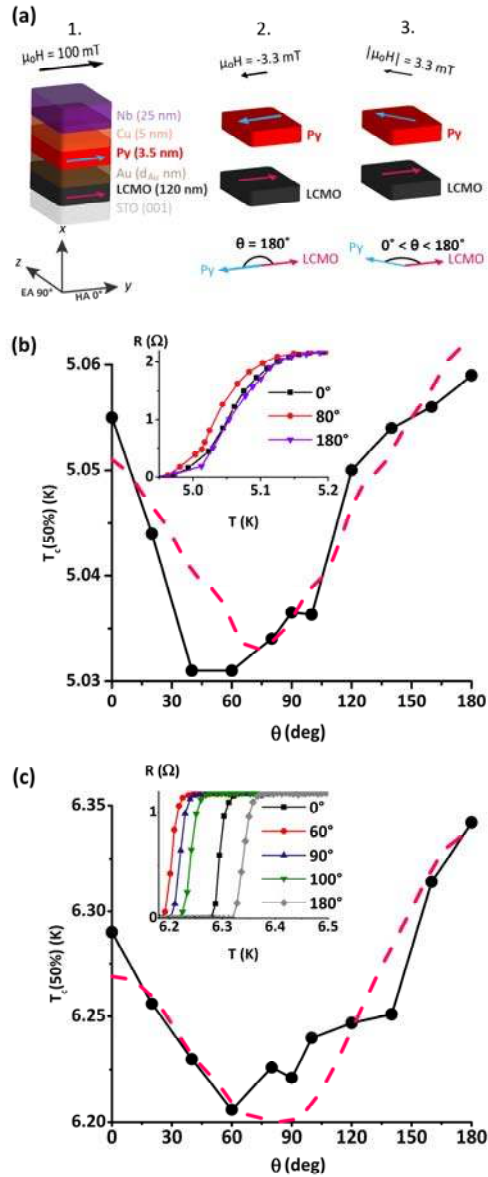
**Fig. 1.** (a)  $M(H)$  loops of LCMO for orthogonal in-plane fields at 10 K. (b)  $M(H)$  of Py with the field parallel to the easy axis (EA) and hard axis (HA). (c)  $M(H)$  loop of a complete TSV which is dominated by the magnetization from the 120-nm-thick LCMO and hence the Py loop (EA) reproduced from (b) is shown for comparison.

### III. RESULTS & DISCUSSION

Figure 2(b) shows  $T_c(\theta)$  for a TSV in which the Au layer has not been etched. Comparing P- and AP-states, we see a standard (albeit small) singlet spin-valve effect with  $T_c(\text{AP}) - T_c(\text{P})$  close to 10 mK. For angles in the  $0^\circ < \theta < 180^\circ$  range,  $T_c(\theta)$  decreases to a local minima of 5.32 K, close to  $\theta = 60^\circ$  giving a maximum  $T_c$  suppression (defined as  $\Delta T_c(\theta) = T_c(\text{AP}) - T_c(\theta)$ ) of -28 mK, which is smaller than the average superconducting transition width. To check that  $T_c(\theta)$  cannot be attributed to potential effects arising from field non-uniformity on  $T_c$  as the TSV is rotated in-plane during measurements of  $R(T)$  (e.g. if the sample is not mounted perfectly parallel to the applied field), we investigated  $T_c(\theta)$  of the Nb(25nm)/Cu(5nm)/Py(3.5nm)/Au(5nm) control sample with the field applied in-plane and tilted out-of-plane by  $10^\circ$  (see Fig. 2S). A maximum  $\Delta T_c(\theta)$  of 10 mK (matching the temperature stability of our system) was observed with no dependence of  $T_c$  on  $\theta$ , meaning that the functional form of  $\Delta T_c(\theta)$  in Fig. 2(b) is related to the relative magnetizations of Py and LCMO and not field non-uniformity.

The small maximum value of  $\Delta T_c(\theta)$  (-28 mK) seen in Fig. 2(b) indicates low interfacial transparency at the Py/Au or Au/LCMO interfaces although we note that  $R(T)$  does not show anomalous features in the superconducting transition, suggesting a homogeneous interfacial resistance (heterogeneous transparency would result in currents paths changing direction through the superconducting transition so as to preferentially flow in superconducting regions). To improve the Py/Au interface,

we Ar-ion etched the Au in situ prior to the sputter-deposition of Nb/Cu/Py and investigated  $\Delta T_C(\theta)$  on etching time (the Au etch rate is  $0.75 \pm 0.04$  nm/min). The largest  $\Delta T_C(\theta)$  of -140 mK (Fig. 2(c)) was achieved for an etch time of 2 minutes with no observable dependence of  $T_C$  on  $\theta$  for an etch time of 8 minutes. These data indicate that increasing the etch time has the effect of improving the interface transparency between Py and Au with  $\Delta T_C(\theta)$  increasing by 110 mK. Simultaneous, etching had the effect of enhancing the singlet spin-valve effect with  $T_C(\text{AP}) - T_C(\text{P})$  increasing from 10 mK (without etching) to 40 mK after 2 minutes of etching (Fig. 3). Over etching the Au, however, risks introducing roughness and ferromagnetic coupling between Py and LCMO and so a decrease in  $\Delta T_C(\theta)$  beyond a certain etch time is expected (as seen for an etch time of 8 minutes). We note that, we also investigated using Cu as an alternative to Au at the LCMO interface, but only a singlet spin-valve effect was observed ( $T_C(\text{AP}) > T_C(\text{P})$ ); see Supplemental Materials for further details.



**Fig. 2.** (a) Measurement sequence to measure  $T_C$  as a function of  $\theta$ . The blue and pink arrows show the likely magnetization configuration of Py and LCMO. (b) and (c) show example data of  $T_C(50\%)$  vs  $\theta$  for Nb(25nm)/Cu(5nm)/Py(3.5nm)/Au( $d_{Au}$ )/LCMO(120nm) TSVs without etching of Au ((b);  $d_{Au}=5$ nm) and following two minutes of etching ((c);  $d_{Au}=3.75$ nm). The dashed pink lines show the simulated values of  $T_C(50\%)$ . The insets show selected  $R(T)$  transitions for various magnetization angles (labelled).

256 To compare our results to theory, we calculated  $\Delta T_C(\theta)$  of the Nb/Cu/Py/Au/LCMO TSVs using a fully  
 257 microscopic procedure, based on numerical solutions to the self-consistent Bogoliubov-de Gennes  
 258 (BdG) equations, as extensively discussed in [18, 19, 58]. Each layer is assumed to be infinite in the  $y$ -  
 259  $z$  plane (see Fig. 2(a)). The four interfaces between Nb and LCMO will have differing transparencies  
 260 and to account for spin-independent scattering at these interfaces, we include repulsive delta  
 261 function potentials  $H_i\delta(x-x_i)$  at each interface position  $x_i$  (where  $i = 1-4$  refers to the interface number:  
 262  $i = 1$  corresponds to the Nb/Cu interface while  $i = 4$  the Cu/LCMO interface). The scattering strength  
 263 is parameterized in dimensionless units by the quantity  $H_{Bi}$ , written as  $H_{Bi}=mH_i/k_F$ , where  $k_F$  is the  
 264 Fermi wavevector, and  $m$  is the effective mass. Thus, increasing  $H_{Bi}$  decreases the interface  
 265 transparency<sup>18,19</sup>. To effectively characterize the TSV and maintain a tractable parameter space, it is  
 266 necessary to keep the scattering strength combinations as simple as possible. We found good  
 267 correlation with experiment when setting  $H_{B1} = H_{B3} = 0.2$  for the Au/LCMO and Cu/Py interfaces  
 268 respectively. For the unetched TSV in (b), we assume a lower transparency at the Py/Au interface  
 269 with  $H_{B2} = 1.2$ , while the Nb/Cu interface is represented with  $H_{B4} = 0.14$ . Using these optimised  
 270 parameters, the model is able to capture the experimental  $T_C(\theta)$  behavior seen in Fig. 4 where the  
 271 local minima in  $T_C$  theoretically relates to the transfer of spin-polarized triplet pairs to LCMO (see also  
 272 Supplementary Material).

273  
 274 It is interesting to note that the experimental and theoretical minimum in  $T_C(\theta)$  are shifted from the  
 275 orthogonal magnetic configuration ( $\theta = 90^\circ$ ). Properly accounting for proximity effects can alter the  
 276 traditional simple view of the triplet spin valve, whereby the equal spin triplet components undergo  
 277 a maximum at 90 degrees (leading to a corresponding dip in  $T_C$ ). By including interface scattering, the  
 278 quasiparticle amplitudes can undergo phase shifts that push the minimum in  $T_C$  away from  $90^\circ$ . The  
 279 same effect also arises in the ballistic regime [18] from the superposition of quasiparticle interactions  
 280 with the interfaces and outer system walls that causes equal spin triplet pair amplitudes to be largest  
 281 at relative magnetization angles away from  $90^\circ$ . See also [58] where similar effects are found in the  
 282 diffusive regime.

283  
 284  
 285  
 286  
 287  
 288  
 289  
 290  
 291  
 292  
 293  
 294  
 295  
 296  
 297  
 298  
 299  
 300

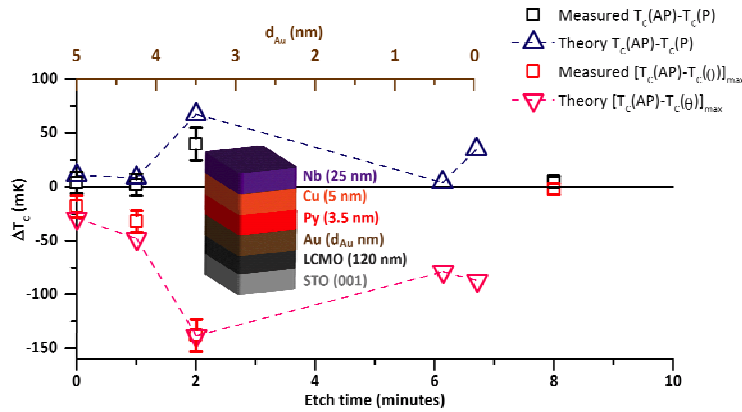


Fig. 3. Theory and experimental  $\Delta T_C$  vs etch Au etch time and Au layer thickness.

301 In Fig. 3, we have compared the experimental and calculated dependence of the maximum value of  
 302  $\Delta T_C(\theta)$  as a function of etching time. To focus on the effect of etching time on the Py/Au interface, we  
 303 fix all interface scattering parameters, except  $H_{B2}$  (relating to the Py/Au interface) which is allowed to  
 304 vary in such a way that is consistent with the measured etch rate. Namely, we set  $H_{B1} = H_{B3} = 0.4$ ,  $H_{B4}$   
 305  $= 0.14$ , and  $0.7 \leq H_{B2} \leq 1.2$ . After a certain time, continued etching is assumed to have no further  
 306 effect on the interface scattering parameter  $H_{B2}$ . The thickness of the Au, however, decreases (0.75

307 nm/min) with etching. For each datum point, we self consistently calculate  $T_c(\theta)$  and extract  $\Delta T_c$  and  
308  $T_c(AP)-T_c(P)$ . This results in good agreement with the experimental findings. In particular, the spin  
309 valve effect is enhanced for an etching time of 2 minutes whereby an increased singlet-to-triplet pair  
310 conversion takes place. Since the normal metal layers tend to host spin-polarised triplet pairs,  
311 reducing their thickness can also result in a limited  $T_c$  reduction that signifies the emergence of spin  
312 polarized triplet pairs.

313  
314  
315  
316

#### IV. SUMMARY

317 We have demonstrated triplet pair creation through magnetization control in Nb/Cu/Py/Cu/LCMO  
318 TSVs using in-plane magnetic field as small as 3.3 mT. Efficient pair conversion and spin-polarized  
319 triplet pair transfer to LCMO is achieved for relative magnetization angles between  $60^\circ$  to  $90^\circ$  with a  
320 maximum  $\Delta T_c(\theta)$  close to -150 mK through band matching optimization at the Au/LCMO interface.  
321 Although  $\Delta T_c(\theta)$  is smaller than observed for TSVs containing  $\text{CrO}_2$  which achieved -800 mK [34]) in an  
322 out-of-plane magnetic fields of 2 T, our results agree well with a fully microscopic self-consistent  
323 model and demonstrate that the fully spin-polarized and chemically stable mixed valance manganites  
324 are highly attractive for superconducting spintronics.

325  
326  
327

#### ACKNOWLEDGEMENTS

328 The work was funded by the Royal Society ('Superconducting Spintronics'), the Leverhulme Trust (IN-  
329 2013-033), and the EPSRC through the Programme Grant "Superspin" (EP/N017242/1) and the  
330 "International network to explore novel superconductivity at advanced oxide  
331 superconductor/magnet interfaces and in nanodevices" Grant (EP/P026311/1) and Doctoral Training  
332 Programme (EP/M508007/1). J.W.A.R. and A.D.B. acknowledge support from St John's College,  
333 Cambridge. Alidoust is supported by Iran's National Elites Foundation (INEF). K.H. is supported in part  
334 by ONR and a grant of HPC resources from the DOD HPCMP.

335

- 336 [1] J. Linder and J.W.A. Robinson, Superconducting spintronics, Nat. Phys. **11**, 4, 307–315 (2015).  
337 [2] M. Eschrig, Spin-polarized supercurrents for spintronics: a review of current progress, Rep. Prog.  
338 Phys. **78**, 10, 104501 (2015).  
339 [3] M.G. Blamire and J.W.A. Robinson, The interface between superconductivity and magnetism:  
340 understanding and device prospects, J. Phys. Condens. Matter **26**, 45, 453201 (2014).  
341 [4] T. Kontos, M. Aprili, J. Lesueur, F. Genêt, B. Stephanidis, and R. Boursier, Josephson Junction  
342 through a Thin Ferromagnetic Layer: Negative Coupling, Phys. Rev. Lett. **89**, 13, 137007 (2002).  
343 [5] Y. Blum, A. Tsukernik, M. Karpovski, and A. Palevski, Oscillations of the Superconducting Critical  
344 Current in Nb-Cu-Ni-Cu-Nb Junctions, Phys. Rev. Lett. **89**, 18, 187004 (2002).  
345 [6] J.W.A. Robinson, S. Piano, G. Burnell, C. Bell, and M.G. Blamire, Critical Current Oscillations in  
346 Strong Ferromagnetic  $\pi$  Junctions, Phys. Rev. Lett. **97**, 17, 177003 (2006).  
347 [7] V. Shelukhin, A. Tsukernik, M. Karpovski, *et al.*, Observation of periodic  $\pi$ -phase shifts in  
348 ferromagnet-superconductor multilayers, Phys. Rev. B **73**, 17, 174506 (2006).  
349 [8] F. Born, M. Siegel, E.K. Hollmann, *et al.*, Multiple  $0 - \pi$  transitions in  
350 superconductor/insulator/ferromagnet/superconductor Josephson tunnel junctions, Phys. Rev. B  
351 **74**, 14, 140501 (2006).  
352 [9] S. Piano, J.W.A. Robinson, G. Burnell, and M.G. Blamire,  $0-\pi$  oscillations in nanostructured  
353 Nb/Fe/Nb Josephson junctions, Eur. Phys. J. B **58**, 2, 123–126 (2007).  
354 [10] J.W.A. Robinson, Z.H. Barber, and M.G. Blamire, Strong ferromagnetic Josephson devices  
355 with optimized magnetism, Appl. Phys. Lett. **95**, 19, 192509 (2009).  
356 [11] Y. Maeno, H. Hashimoto, K. Yoshida, *et al.*, Superconductivity in a layered perovskite without  
357 copper, Nature, **372**, 6506, 532–534 (1994).



- 358 [12] A.P. Mackenzie, R.K.W. Haselwimmer, A.W. Tyler, *et al.*, Extremely Strong Dependence of  
359 Superconductivity on Disorder in  $\text{Sr}_2\text{RuO}_4$ , *Phys. Rev. Lett.* **8**, 1, 161–164 (1998).
- 360 [13] F.S. Bergeret, A.F. Volkov, and K.B. Efetov, Odd triplet superconductivity and related  
361 phenomena in superconductor-ferromagnet structures, *Rev. Mod. Phys.* **77**, 4, 1321–1373 (2005);  
362 *ibid.*, *Rev. Mod. Phys.* **77**, 1321 (2005).
- 363 [14] B.W. Maxfield and W.L. McLean, Superconducting Penetration Depth of Niobium, *Phys. Rev.*  
364 **139**, 5A, A1515–A1522 (1965).
- 365 [15] V.V. Ryazanov, Josephson superconductor—ferromagnet—superconductor  $\pi$ -contact as an  
366 element of a quantum bit (experiment), *Phys.-Uspekhi* **42**, 8, 825–827 (1999).
- 367 [16] T. Kontos, M. Aprili, J. Lesueur, and X. Grison, Inhomogeneous Superconductivity Induced in a  
368 Ferromagnet by Proximity Effect, *Phys. Rev. Lett.* **86**, 2, 304–307 (2001).
- 369 [17] Y.V. Fominov, A.A. Golubov, T.Y. Karminskaya, M.Y. Kupriyanov, R.G. Deminov, and L.R.  
370 Tagirov, Superconducting triplet spin valve, *JETP Lett.* **91**, 6, 308–313 (2010).
- 371 [18] K. Halterman and M. Alidoust, Half-metallic superconducting triplet spin valve, *Phys. Rev. B*  
372 **94**, 6, 064503 (2016).
- 373 [19] M. Alidoust, K. Halterman, and O.T. Valls, Zero-energy peak and triplet correlations in  
374 nanoscale superconductor/ferromagnet/ferromagnet spin valves, *Phys. Rev. B* **92**, 1, 014508  
375 (2015).
- 376 [20] M. Alidoust and K. Halterman, Proximity induced vortices and long-range triplet  
377 supercurrents in ferromagnetic Josephson junctions and spin valves, *J. Appl. Phys.* **117**, 12,  
378 123906 (2015).
- 379 [21] J.W.A. Robinson, J.D.S. Witt, and M.G. Blamire, Controlled Injection of Spin-Triplet  
380 Supercurrents into a Strong Ferromagnet, *Science* **329**, 5987, 59–61 (2010); see also G. B. Halasz,  
381 M. G. Blamire, and J. W. A. Robinson, *Phys. Rev. B* **84**, 024517 (2011) and J. W. A. Robinson, F.  
382 Chiodi, M. Egilmez, Gábor B. Halász, and M. G. Blamire, *Sci. Rep.* **2**, 699 (2012).
- 383 [22] J.D.S. Witt, J.W.A. Robinson, and M.G. Blamire, Josephson junctions incorporating a conical  
384 magnetic holmium interlayer, *Phys. Rev. B* **85**, 18, 184526 (2012).
- 385 [23] J.W.A. Robinson, N. Banerjee, and M.G. Blamire, Triplet pair correlations and nonmonotonic  
386 supercurrent decay with Cr thickness in Nb/Cr/Fe/Nb Josephson devices, *Phys. Rev. B* **89**, 10,  
387 104505 (2014); see also J. W. A. Robinson, G. B. Halász, A. I. Buzdin, and M. G. Blamire, *Phys.*  
388 *Rev. Lett.* **104**, 207001 (2010).
- 389 [24] D. Sprungmann, K. Westerholt, H. Zabel, M. Weides, and H. Kohlstedt, Evidence for triplet  
390 superconductivity in Josephson junctions with barriers of the ferromagnetic Heusler alloy  
391  $\text{Cu}_2\text{MnAl}$ , *Phys. Rev. B* **82**(6), 060505 (2010).
- 392 [25] T.S. Khaire, M.A. Khasawneh, W.P. Pratt, and N.O. Birge, Observation of Spin-Triplet  
393 Superconductivity in Co-Based Josephson Junctions, *Phys. Rev. Lett.* **104**, 13, 137002 (2010).
- 394 [26] C. Klose, T.S. Khaire, Y. Wang, *et al.*, Optimization of Spin-Triplet Supercurrent in  
395 Ferromagnetic Josephson Junctions, *Phys. Rev. Lett.* **108**, 12, 127002 (2012).
- 396 [27] M.S. Anwar, M. Veldhorst, A. Brinkman, and J. Aarts, Long range supercurrents in  
397 ferromagnetic  $\text{CrO}_2$  using a multilayer contact structure, *Appl. Phys. Lett.* **100**, 5, 052602 (2012).
- 398 [28] N. Banerjee, J.W.A. Robinson, and M.G. Blamire, Reversible control of spin-polarized  
399 supercurrents in ferromagnetic Josephson junctions, *Nat. Commun.* **5**, 4771 (2014).
- 400 [29] W.M. Martinez, W.P. Pratt, and N.O. Birge, Amplitude Control of the Spin-Triplet  
401 Supercurrent in S / F / S Josephson Junctions, *Phys. Rev. Lett.* **116**, 7, 077001 (2016).
- 402 [30] P.V. Leksin, N.N. Garif'yanov, I.A. Garifullin, *et al.*, Evidence for Triplet Superconductivity in a  
403 Superconductor-Ferromagnet Spin Valve, *Phys. Rev. Lett.* **109**, 5, 057005 (2012).
- 404 [31] V.I. Zdravkov, J. Kehrle, D. Lenk, *et al.*, Reentrant superconductivity and superconducting  
405 critical temperature oscillations in F/S/F trilayers of  $\text{Cu}_{41}\text{Ni}_{59}/\text{Nb}/\text{Cu}_{41}\text{Ni}_{59}$  grown on cobalt oxide,  
406 *J. Appl. Phys.* **114**, 3, 033903 (2013).
- 407 [32] X.L. Wang, A. Di Bernardo, N. Banerjee, *et al.*, Giant triplet proximity effect in  
408 superconducting pseudo spin valves with engineered anisotropy, *Phys. Rev. B* **89**, 14, 140508  
409 (2014).

- 410 [33] P.V. Leksin, N.N. Garif'yanov, A.A. Kamashev, *et al.*, Superconducting spin-valve effect and  
411 triplet superconductivity in  $\text{CoO}_x/\text{Fe}_1/\text{Cu}/\text{Fe}_2/\text{Cu}/\text{Pb}$  multilayer, *Phys. Rev. B* **91**, 21, 214508  
412 (2015).
- 413 [34] A. Singh, S. Voltan, K. Lahabi, and J. Aarts, Colossal Proximity Effect in a Superconducting  
414 Triplet Spin Valve Based on the Half-Metallic Ferromagnet  $\text{CrO}_2$ , *Phys. Rev. X* **5**, 2, 021019 (2015).
- 415 [35] I.C. Moraru, W.P. Pratt, and N.O. Birge, Magnetization-Dependent  $T_C$  Shift in  
416 Ferromagnet/Superconductor/Ferromagnet Trilayers with a Strong Ferromagnet, *Phys. Rev. Lett.*  
417 **96**, 3, 037004 (2006).
- 418 [36] J.Y. Gu, C.-Y. You, J.S. Jiang, J. Pearson, Y.B. Bazaliy, and S.D. Bader, Magnetization-  
419 Orientation Dependence of the Superconducting Transition Temperature in the Ferromagnet-  
420 Superconductor-Ferromagnet System:  $\text{CuNi}/\text{Nb}/\text{CuNi}$ , *Phys. Rev. Lett.* **89**, 26, 267001 (2002).
- 421 [37] Y. Gu, G.B. Halász, J.W.A. Robinson, and M.G. Blamire, Large Superconducting Spin Valve  
422 Effect and Ultrasmall Exchange Splitting in Epitaxial Rare-Earth-Niobium Trilayers, *Phys. Rev. Lett.*  
423 **115**, 6, 067201 (2015).
- 424 [38] K.A. Yates, L.A.B. Olde Olthof, M.E. Vickers, *et al.*, Andreev bound states in  
425 superconductor/ferromagnet point contact Andreev reflection spectra, *Phys. Rev. B* **95**, 9,  
426 094516 (2017).
- 427 [39] A. Di Bernardo, Z. Salman, X.L. Wang, *et al.*, Intrinsic Paramagnetic Meissner Effect Due to s -  
428 Wave Odd-Frequency Superconductivity, *Phys. Rev. X* **5**(4), 041021 (2015).
- 429 [40] A. Di Bernardo, S. Dirsch, Y. Gu, *et al.*, Signature of magnetic-dependent gapless odd  
430 frequency states at superconductor/ferromagnet interfaces, *Nat. Commun.* **6**, 8053 (2015).
- 431 [41] Y. Kalcheim, O. Millo, A. Di Bernardo, A. Pal, and J.W.A. Robinson, Inverse proximity effect at  
432 superconductor-ferromagnet interfaces: Evidence for induced triplet pairing in the  
433 superconductor, *Phys. Rev. B* **92**, 6, 060501(R) (2015).
- 434 [42] Y. Kalcheim, I. Felner, O. Millo, *et al.*, Magnetic field dependence of the proximity-induced  
435 triplet superconductivity at ferromagnet/superconductor interfaces, *Phys. Rev. B* **89**, 18, 180506  
436 (2014).
- 437 [43] Y. Kalcheim, O. Millo, M. Egilmez, J.W.A. Robinson, and M.G. Blamire, Evidence for  
438 anisotropic triplet superconductor order parameter in half-metallic ferromagnetic  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$   
439 proximity coupled to superconducting  $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ , *Phys. Rev. B* **85**, 10, 104504 (2012).
- 440 [44] C. Visani, Z. Sefrioui, J. Tornos, *et al.*, Equal-spin Andreev reflection and long-range coherent  
441 transport in high-temperature superconductor/half-metallic ferromagnet junctions, *Nat. Phys.* **8**,  
442 7, 539–543 (2012).
- 443 [45] I.T.M. Usman, K.A. Yates, J.D. Moore, *et al.*, Evidence for spin mixing in holmium thin film and  
444 crystal samples, *Phys. Rev. B* **83**, 14, 144518 (2011).
- 445 [46] K.M. Boden, W.P. Pratt, and N.O. Birge, Proximity-induced density-of-states oscillations in a  
446 superconductor/strong-ferromagnet system, *Phys. Rev. B* **84**, 2, 020510(R) (2011).
- 447 [47] Y. Kalcheim, T. Kirzhner, G. Koren, and O. Millo, Long-range proximity effect in  $\text{La}_{2/3}\text{Ca}$   
448  $_{1/3}\text{MnO}_3/(\text{100})\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ferromagnet/superconductor bilayers: Evidence for induced triplet  
449 superconductivity in the ferromagnet, *Phys. Rev. B* **83**, 6, 064510 (2011).
- 450 [48] P. SanGiorgio, S. Reymond, M.R. Beasley, J.H. Kwon, and K. Char, Anomalous Double Peak  
451 Structure in Superconductor/Ferromagnet Tunneling Density of States, *Phys. Rev. Lett.* **100**, 23,  
452 237002 (2008).
- 453 [49] R.S. Keizer, S.T.B. Goennenwein, T.M. Klapwijk, G. Miao, G. Xiao, and A. Gupta, A spin triplet  
454 supercurrent through the half-metallic ferromagnet  $\text{CrO}_2$ , *Nature* **439**, 7078, 825–827 (2006).
- 455 [50] J.Y.T. Wei, N.-C. Yeh, and R.P. Vasquez, Tunneling Evidence of Half-Metallic Ferromagnetism  
456 in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ , *Phys. Rev. Lett.* **79**, 25, 5150–5153 (1997).
- 457 [51] Y. Okimoto, T. Katsufuji, T. Ishikawa, A. Urushibara, T. Arima, and Y. Tokura, Anomalous  
458 Variation of Optical Spectra with Spin Polarization in Double-Exchange Ferromagnet:  
459  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , *Phys. Rev. Lett.* **75**, 1, 109–112 (1995).

460 [52] M. Egilmez, J.W.A. Robinson, J.L. MacManus-Driscoll, L. Chen, H. Wang, and M.G. Blamire,  
461 Supercurrents in half-metallic ferromagnetic  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ , EPL Europhys. Lett. **106**, 3, 37003  
462 (2014).  
463 [53] C. Visani, F. Cuellar, A. Pérez-Muñoz, *et al.*, Magnetic field influence on the proximity effect  
464 at  $\text{YBa}_2\text{Cu}_3\text{O}_7/\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  superconductor/half-metal interfaces, Phys. Rev. B **92**, 1, 014519  
465 (2015).  
466 [54] P.R. Sagdeo, S. Anwar, and N.P. Lalla, Powder X-ray diffraction and Rietveld analysis of  
467  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ , Powder Diffr. **21**, 1, 40–44 (2006).  
468 [55] See Supplemental Material at [URL will be inserted by publisher].  
469 [56] S. Valencia, Z. Konstantinovic, D. Schmitz, A. Gaupp, L. Balcells, and B. Martínez, Interfacial  
470 effects in manganite thin films with different capping layers of interest for spintronic applications,  
471 Phys. Rev. B **84**, 2, 024413 (2011).  
472 [57] A. Wallraff, D.I. Schuster, A. Blais, *et al.*, Approaching Unit Visibility for Control of a  
473 Superconducting Qubit with Dispersive Readout, Phys. Rev. Lett. **95**, 6, 060501 (2005).  
474 [58] P.H. Barsic, O.T. Valls, and K. Halterman, Thermodynamics and phase diagrams of layered  
475 superconductor/ferromagnet nanostructures, Phys. Rev. B **75**, 10, 104502 (2007).  
476 [59] R. Yang, X. M. Li, W. D. Yu, X. D. Gao, D. S. Shang, X. J. Liu, X. Cao, Q. Wang, and L. D. Chen,  
477 Appl. Phys. Lett. **95**, 72105 (2009).  
478  
479  
480  
481