Supercurrents through half-metallic ferromagnetic \( \text{CrO}_2 \) revisited

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(Dated: March 24, 2010)

We report on the observation of a supercurrent through the half metallic ferromagnet \( \text{CrO}_2 \) grown on hexagonal \( \text{Al}_2\text{O}_3 \) (sapphire). The current was observed to flow over a distance of 700 nm between two superconducting amorphous \( \text{Mo}_{70}\text{Ge}_{30} \) electrodes which were deposited on the \( \text{CrO}_2 \) film. The critical current \( I_c \) increases as function of decreasing temperature. Upon applying an in-plane magnetic field, \( I_c \) goes through a maximum at the rather high field of 80 mT. We believe this to be a long range proximity effect in the ferromagnet, carried by odd-frequency pairing correlations.

PACS numbers: 74.45.+c, 74.50.+r, 75.70.Cn, 72.25.Mk, 73.40.-c

Conventional superconductivity is generally assumed to decay rapidly inside a ferromagnet since the spin singlet Cooper pairs are broken up by the exchange field \( \hbar \omega \) when the pair diffuses through the superconductor (S)/ferromagnet (F) interface. In the dirty limit, the decay length \( \xi_F \propto 1/\sqrt{\hbar \omega} \) is no more than 10 nm even for a weak ferromagnet. Another type of pair correlations is also possible in the magnet, based on spin triplets. These correlations have orbital \( p \)-symmetry conformation to the Pauli principle \([1]\), are only sustained in clean systems, and can lead to a long range proximity (LRP) effect. However, it was argued that, under the principle of odd-frequency pairing, even \( s \)-symmetry is possible \([2, 3]\). Such correlations can even exist in dirty systems, and would also be long ranged in the ferromagnet. To produce odd frequency triplets in the magnet, two mechanisms were proposed. One is that the singlets on the S-side of the interface sample an inhomogeneous magnetization on the F-side \([2, 3]\). The other is a two-step process in which differences in spin scattering at the S/F interface first cause spin mixing in the Cooper pair singlet, leading to \( m = 0 \) triplet correlations. Magnetic disorder then can produce the required spin triplet component \([4]\). The latter mechanism can be particularly relevant when the magnet is fully spin-polarized (a so-called half-metallic ferromagnet), since in that case triplet correlations cannot be broken by spin flip scattering. The decay length is then set by thermal dephasing as in the case of normal metals, and can become very long ranged.

Experimental indications for the LRP effect do exist. Sosnin \textit{et al.}, using an Andreev interferometer geometry, reported supercurrents flowing in ferromagnetic Ho wires with lengths up to 150 nm \([5]\); around the same time, Keizer \textit{et al.} reported supercurrents induced in the half-metallic ferromagnet \( \text{CrO}_2 \) when superconducting electrodes of \( \text{NbTiN} \) were placed on the unstructured film, with separations up to 1 \( \mu \text{m} \) \([6]\). Even for normal metals this can be considered a very long range. Very recently, Khaire \textit{et al.} prepared Josephson junctions with ferromagnetic Cobalt, and found no decay of the value of the Josephson current up to a thickness of 30 nm of the Co layer \([7]\).

Neither Ho nor Co are fully spin polarized, and the triplet decay will be set by the spin diffusion length, which is 100 nm (order of magnitude) in both materials. That makes the \( \text{CrO}_2 \) case with its significantly larger decay length of special interest, but here the issue of reproducibility has hampered progress. The original report mentioned large variations in the magnitude of the critical (super)current \( I_c \) between different samples, while not all samples showed the effect \([8]\); no other reports on experiments with \( \text{CrO}_2 \) have been published.

In this Letter we report new observations of supercurrents in \( \text{CrO}_2 \). The devices we studied are different from the earlier ones in various aspects. In particular, we have grown \( \text{CrO}_2 \) films on \( \text{Al}_2\text{O}_3 \) (sapphire) rather than on \( \text{TiO}_2 \), which leads to significant differences in film morphology; and the superconducting contacts are made from amorphous (\( a \)-)\( \text{Mo}_{70}\text{Ge}_{30} \), rather than from \( \text{NbTiN} \). Again we find significant values for \( I_c \) even at a separation of about 1 \( \mu \)m between the electrodes, and only small sensitivity to applied magnetic fields up to 0.5 T.

A special issue in the device preparation lies in the growth of \( \text{CrO}_2 \) films. Bulk \( \text{CrO}_2 \) is a metastable phase and is synthesized at high oxygen pressures. Low-pressure film growth techniques such as sputtering, pulsed laser deposition, or molecular beam epitaxy therefore cannot be used. Still, high-quality films can be grown by chemical vapor deposition (CVD) at ambient pressure. For this a precursor is used (\( \text{CrO}_3 \)), which is heated in a furnace with flowing oxygen that transports the sublimated precursor to a substrate at an elevated temperature, where it decomposes and forms \( \text{CrO}_2 \). The method only works well, however, for substrates with lattice parameters closely matching the \( b \)-axis of the tetragonal \( \text{CrO}_2 \) (\( b = 0.4421 \) nm), such as \( \text{TiO}_2(100) \) (quasi-orthogonal with \( b = 0.4447 \) nm) or \( \text{Al}_2\text{O}_3(0001) \) (hexagonal with \( a = 0.4754 \) nm), for
which the method was specifically demonstrated [8,9]. For our experiments, films were grown on both types of substrates in the manner described above, with the precursor at 260 °C, substrates at 390 °C, and an oxygen flow of 100 sccm. Deposition on TiO$_2$ leads to films with a morphology widely different from films grown on Al$_2$O$_3$, as can be seen from the images in Fig. 1 made by atomic force microscopy. The TiO$_2$ substrate has an almost square surface net, and the film structure consists of (elongated) platelets as was shown earlier [10]. The hexagonal structure of Al$_2$O$_3$ leads to growth of crystallites along all 6 major axes, and to considerably more surface roughness. An important point to make is that growth on Al$_2$O$_3$ does not start as CrO$_2$, but as Cr$_2$O$_3$, which is isostructural to the sapphire. Only after a layer of about 40 nm has been deposited, the growing film becomes CrO$_2$ as found in Ref. [11]. Using Transmission Electron Microscopy, our finding is similar, (Fig. 2a). The Cr$_2$O$_3$ layer is visible as a dark band of about 30 nm adjacent to the substrate, followed by a brighter area of about 100 nm which is the CrO$_2$ film . The dark band on top is the a-Mo$_{70}$Ge$_{30}$ used as superconducting contact. Also visible is the columnar structure of the film. Since it is difficult to determine the film thickness from a calibrated deposition time, we used the magnetic properties instead. Cr$_2$O$_3$ is an antiferromagnetic insulator and CrO$_2$ a ferromagnetic metal with a magnetic moment of 2.0 $\mu_B$/Cr-atom ($\mu_B$ is the Bohr magneton), and the measured magnetic moment was used to calculate the CrO$_2$ thickness. The films were characterized by electrical transport measurements. Both specific resistance and saturation magnetization behave as expected, with the (low temperature) residual resistivity $\rho_0 = 7 \times 10^2 \mu\Omega$ cm for films on TiO$_2$ (Al$_2$O$_3$). The insulating nature of the substrates is an impediment in lithography. In particular it is difficult to etch a structure into the film and then define electrodes on the bare substrate with electron beam lithography.

Instead, we made the devices by (RF-)sputtering 60 nm of (a-)Mo$_{70}$Ge$_{30}$ superconducting electrodes with a superconducting transition temperature $T_c \approx 6.5$ K through a lift-off mask onto the unstructured film. Before the deposition, the film surface was cleaned briefly with an O$_2$ reactive ion plasma, in order to remove resist or developer residues. Ar-ion etching was applied immediately prior to deposition, in order to remove newly formed Cr$_2$O$_3$ on the film surface. The width of the electrodes was about 30 $\mu$m, and the gap between the electrodes around 700 nm. Fig. 2b,c show the layout of the electrodes on the film surface and an electron microscopy image of the gap.

A number of devices were prepared in this way, and 3 out of roughly 10 showed a supercurrent. We call them A,B, and C; device B was slightly different from the other two in that it consisted of three parallel electrodes rather than one, with a distance between electrodes of 100 $\mu$m, and the three gaps measured in parallel. Fig. 4 shows the current-voltage ($I$-$V$) characteristic of device A, taken between 6 K (just below $T_c$) and 2.5 K. We observe a clear zero resistance supercurrent branch, with a maximum value for $I_c$ of 170 $\mu$A at 2.5 K. The inset shows data for device B measured at 2 K. From these measurements $I_c$ was determined as the first deviation from the linear $I$-$V$ characteristic around zero bias (equivalent to the peak in the derivative $dI/dV$). The temperature dependence $I_c(T)$ is given in Fig. 4 for all three samples. All devices have very similar values for the critical current, even for the case of three parallel electrodes. The behavior close to $T_c$ is concave rather than linear. In Fig. 5 we present the effect of applying a magnetic field $H_a$ on $I_c$ in device A at a temperature of 3 K. The field was applied in the plane of the film, with a direction either parallel to the long axis of the electrodes (not shown), or perpendicular to that axis. In the first configuration we do not find effects up to 500 mT. In

FIG. 1: (Color online) Atomic Force Microscopy images of CrO$_2$ films grown on (a) a TiO$_2$ substrate; the (001) axis of the substrate is indicated; (b) an Al$_2$O$_3$ substrate. The different directions of the crystallites which are found in the image are indicated with the arrows and seen to make angles of 60°.

FIG. 2: (a) Transmission Electron Microscopy image of a CrO$_2$ film grown on Al$_2$O$_3$. Visible are the substrate, the Cr$_2$O$_3$ seed layer, the CrO$_2$ layer, and the a-Mo$_{70}$Ge$_{30}$ layer. (b) Layout of the device structure with four current / voltage contacts. The width of the electrodes is 30 $\mu$m. (c) Scanning electron Microscopy image of the gap between the two electrodes, made by lift-off.
the second configuration we find large changes, however. Starting from zero field, $I_c$ increases by about 10% and goes through a maximum around 80 mT before dropping down to a level which at 500 mT is about 10% below the zero field value. Sweeping back, the behavior is different, with a relatively sharp jump back to the zero field level, but no peak as in the forward sweep. Continuing in the negative field quadrant, no structure in $I_c$ is found. A point to note is that the maximum lies well outside the hysteresis loop of the magnet. The coercive field $H_c$ are of the order of 10 mT only (inset of Fig. 3). Unfortunately, the samples proved fragile and could only be cooled down a few times before the supercurrent disappeared, although there was no slow degradation as long as the supercurrent was present.

The results are best discussed in comparison with the previous report on supercurrents in CrO$_2$ [6]. Firstly, we can compare their magnitudes by assuming that the current flows homogeneously across the bridge and through the full thickness $d_{CrO_2}$ of the layer. In our case ($d_{CrO_2} \approx 100$ nm, bridge width $30 \mu$m, current $100 \mu$A) we find a critical current density at 2 K of about $3 \times 10^7$ [A/m$^2$]. The earlier data ($d_{CrO_2} = 100$ nm, bridge width 2 $\mu$m, typical current 1 mA) correspond to $5 \times 10^9$ [A/m$^2$], and from this point of view there appears to be a large difference between the two results. Another way of looking at them is to compare the field dependence. In Ref. [6], a Fraunhofer pattern was detected with a distance between maxima of about 90 mT. Assuming this equivalent to one flux quantum $\Phi_0$ in the junction area of 310 nm $\times$ $d_{CrO_2}$, a value of roughly 80 nm is found for $d_{CrO_2}$, quite close to the nominal thickness and suggesting that the full film thickness is partaking in the supercurrent (e.g. in the shielding from the magnetic field). In the dataset presented here (Fig. 3) a Fraunhofer pattern is not clearly visible, but there is a maximum at 80 mT followed by discontinuities around 150 mT and 250 mT, and a small maximum at 300 mT. Taken together, this suggests a period of 100 mT. For a junction area of 700 nm $\times$ $d_{CrO_2}$, this corresponds to $d_{CrO_2} \approx 30$ nm, which indicates that in our case the current is not flowing through the full thickness of the layer. The picture then emerging is that, although the results are qualitatively the same, the growth on Al$_2$O$_3$ leads to a somewhat weaker junction. Since the TEM picture in Fig. 2 shows that in our devices grain boundaries will always be in the path of the current, this actually seems a reasonable conclusion. Another point to discuss is that the maximum in the Fraunhofer pattern is not found at zero field. In Ref. [6] this was ascribed to the finite sample magnetization. The difficulty here is that, starting from the demagnetized (domain) state, the maximum can be expected when magnetization saturation is reached, which is at a significantly smaller field value. An alternative explanation is that in the case of a triplet supercurrent the junction is expected to show a phase shift of $\pi$ [13, 14]; such a $\pi$-junction would show a minimum at zero-field rather than a maximum.

There is another way to gauge the strength of the junction. According to diffusive theory, $I_c$ for a long S-N-S junction (N a normal metal) is proportional to $T^{3/2} \exp \left( \sqrt{(2\pi k_B T)/(E_{Th})} \right)$, with $E_{Th}$ the Thouless energy given by $(kD/L^2)^2$; here, $D$ is the diffusion constant of the N metal and $L$ the length of the junction [12, 13]. Plotting $\ln(I_c) - 3/2 \ln(T)$ versus $\sqrt{T}$ in the inset of Fig. 3 shows that the relation holds well at low temperatures, with values for $E_{Th}$ of 72 (91) $\mu$V for device A (B, C). This in turn can be used to estimate the maximum critical current from the relation $eI_cR_N = 10.8 E_{Th}$ [13]. The normal resistance $R_N$ of the junction is 11 $\Omega$, which would yield a value for $I_c$ of 75 $\mu$A. Although this compares well to the measurements, the measured $R_N$ does not seem the appropriate value to use, since it is dominated by the contact resistance.
Using a typical specific resistance, measured in various films, of 10 $\mu\Omega$cm, we rather estimate the normal resistance of the junction to be 4 m$\Omega$, which would yield a value for $I_c$ of 200 mA. Although this may be an overestimation, it indicates that the measured values for $I_c$ are actually lower than what can be achieved.

Overall, the numbers suggest in several ways that the junctions are weaker than could be, leading to a discussion of the reproducibility, including the fact that not every device shows a supercurrent. In working devices, the current densities are large enough to conclude that the effect is intrinsic, rather than carried by filamentary normal metal shorts in the ferromagnetic matrix, for which also otherwise no signs exist. Our premise is that the supercurrent is of triplet nature, and a difficulty lies which also otherwise no signs exist. Our premise is that the supercurrent is of triplet nature, and a difficulty lies which also otherwise no signs exist. Our premise is that the triplet generation takes place at isolated spots.

Higher Education Commission (HEC) Pakistan.

We thank T.M. Klapwijk, F. Czeschka, S. Gönnenwein, H. W. Zandbergen and V. Ryazanov for useful discussions. M.S.A. acknowledges the financial support of the Higher Education Commission (HEC) Pakistan.

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