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# Role of the barrier in spin-dependent tunneling addressed with superconductor spectroscopy

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To establish the role of the barrier material in spin-polarized tunneling, we directly measure the sign and magnitude of the tunneling spin polarization in Al/barrier/ferromagnet junctions with different barriers using the Zeeman-split superconducting density of states of the Al electrode. It is shown that clear Zeeman splitting is difficult to obtain with heavy metal oxide barriers, such as $HfO_x$ and $TaO_x$, due to a large spin-orbit scattering rate most likely induced by the heavy atoms at the Al/barrier interface. Junctions with MgO barriers, however, show clear Zeeman splitting and a tunneling spin polarization of $+30\%$ with both Co and Fe as the top electrode, a number which significantly differs from $+40\%$ found for our $AlO_x$ junctions. We claim that this barrier dependence originates from the electronic structure of the barrier/ferromagnet interface. The positive tunneling polarization is consistent with the presumption that due to the absence of *d* orbitals in the MgO barrier, tunneling is dominated by electrons with *s* character.

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Tunneling spin polarization is the key ingredient of the tunnel magnetoresistance (TMR) effect shown by magnetic tunnel junctions,[1] a new class of devices currently under development for magnetic memory and field sensor applications.[2] TMR experiments exploiting different barrier materials have suggested a decisive role of the barrier material for the sign and magnitude of the tunneling spin polarization ($P$). More specific, $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3/Co$ junctions, for example, show a negative TMR effect,[3] which is explained by a negative $P$ of the electrons tunneling from the Co electrode, in contrast with the positive TMR and $P$ found with $AlO_x$ barriers.[4] These kind of experimental TMR results and various theoretical calculations (see, for example, Refs. 5 and 6), have cumulated into a hypothesis which can be summarized by a simple rule of thumb: Barriers which contain *d* orbitals (such as $SrTiO_3$, $TaO_x$, and $HfO_x$) favor tunneling of electrons with *d* character, while barriers without *d* orbitals (such as $AlO_x$ and MgO) favor tunneling of electrons with *s* character. Since the polarization of the density of states of the *d* electrons at the Fermi level in Co is negative, the rule predicts that a negative $P$ is to be expected for $SrTiO_3$, $TaO_x$, and $HfO_x$ barriers.

This role of the barrier material can be studied by TMR experiments, which, however, give only indirect indications of $P$. In contrast, with use of the well-established spin-polarized tunneling (SPT) technique pioneered by Meservey and Tedrow,[4] $P$ can be measured directly. In this technique, $P$ is reflected by the asymmetry in the conductance-voltage ($dI/dV$-$V$) relation measured while the superconducting density of states of an Al counter electrode is Zeeman split by an external magnetic field.

Mostly, SPT has been performed with amorphous $AlO_x$ barriers.[4,7,8] Moodera *et al.*, used SPT to demonstrate the spin-filter effect in junctions with EuS and EuSe barriers.[9,10] Worledge and Geballe performed SPT with $SrTiO_3$ barriers to measure $P$ in $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3/Al$ and $SrRuO_3/SrTiO_3/Al$ junctions,[11,12] and Parker *et al.* measured $CrO_2/Cr_2O_3/Al$ junctions.[13] To date, SPT has not been used to investigate the barrier dependence of $P$ by comparing junctions with a given fixed ferromagnetic electrode and different barriers.

In this paper we present SPT measurements on Al/barrier/ferromagnet junctions with Co and Fe top electrodes and different amorphous barrier materials with a view to address the role of the barrier through direct measurement of $P$. We show that Zeeman splitting of the superconducting density of states is, in principle, difficult to obtain with heavy metal oxide barriers, such as $HfO_x$ and $TaO_x$, due to a large spin-orbit scattering rate in the Al superconductor most likely induced by the heavy atoms at the Al/barrier interface. We demonstrate clear Zeeman splitting in junctions with MgO barriers and measure a significantly different $P$ as compared to $AlO_x$ junctions.

Our tunnel junctions are prepared by magnetron sputtering (base pressure $<10^{-9}$ mbar) through metal shadow masks on glass substrates at room temperature. The $AlO_x$ junctions are obtained by partially oxidizing a 40-Å Al bottom electrode with an *in situ* oxygen plasma ($10^{-1}$ mbar, 5 W) for 200 s. Finally, Co and Fe top electrodes are deposited in a cross-stripe configuration resulting in $400\ \mu m \times 400\ \mu m$ junctions with a resistance-area product of roughly $10^5\ k\Omega\ \mu m^2$.

For the SPT measurements the junctions are cooled to 0.3 K in a sorption-pumped $^3$He cryostat. Current-voltage ($I$-$V$), and conductance-voltage ($dI/dV$-$V$) characteristics are measured in a four-terminal configuration using a standard lock-in technique. Our Al bottom electrodes become superconducting at about 2.2 K and have critical fields of 4.5 T. Figure 1(a) shows a representative conductance measurement of an $Al/AlO_x/Co$ junction. In zero field, the conductance reflects the superconducting density of states with its sharp maxima at the edge of the superconducting band gap. In a field of 3.0 T, applied in plane with the junction, the density of states is Zeeman split and $P$ is directly reflected by the differences in the four maxima.[4] The polarization is extracted by fitting the model based on the Maki theory[14–16] to the in-field measurement. This model accounts for the effect of orbital-depairing and spin-orbit scattering on the superconducting density of states.[4] For the Co and Fe control junctions we find a polarization of $+39\pm1\%$ and $+41\pm1\%$,

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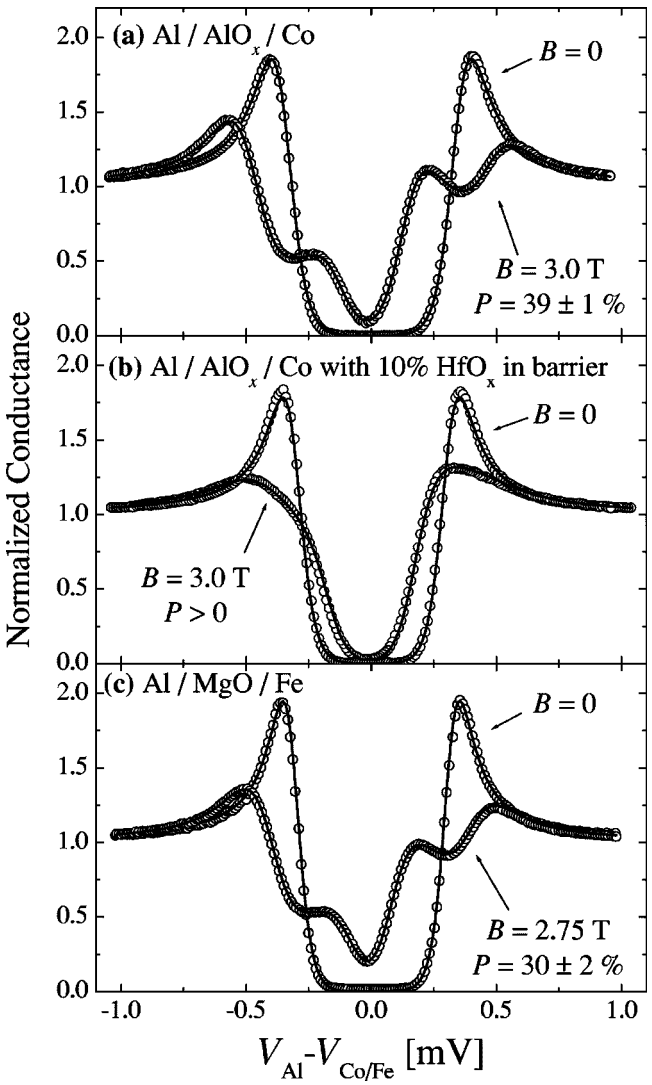


FIG. 1. Representative conductance measurements at 0.3 K of an $Al/AlO_x/Co$ junction (a), an $Al/AlO_x/Co$ junction with $HfO_x$ in the barrier (b), and an Al/MgO/Fe junction (c). The measurements are performed in zero field and an in-plane field of several tesla. The solid lines are theoretical fits.

respectively, with the error margins determined by sample-to-sample variation. These results are in fair agreement with earlier work.[7,8]

To study the barrier dependence of $P$, we replace the $AlO_x$ barrier by another insulator. In general, for clear observation of the Zeeman-split superconducting density of states, the insulator needs to meet two requirements. First, the conduction mechanism should be dominated by single-step tunneling. This is reflected by an increase of the junction resistance during cooling of roughly 50%. This temperature dependence is usually obtained with $AlO_x$ barriers.[17] If the insulator is poor, in the sense that it possesses a thermally activated hopping conductance, for example, the junction resistance increases with orders of magnitude and the conductance does not show the required sharp peaks at the band-gap edge.[18] Second, we claim that the insulator should consist only of elements with a low atomic number. In earlier SPT measurements it has been observed that Zeeman splitting is quenched due to a high spin-orbit scattering rate induced by an amount of heavy impurities present in the Al electrode.[4] We suggest that also heavy atoms at the superconductor/barrier interface induce a high spin-orbit scattering rate. To substantiate this issue, we consider an $Al/AlO_x/Co$ junction containing a small amount (roughly 10%) of the heavy metal oxide $HfO_x$ in the barrier. This junction is prepared by depositing one or two monolayers of Hf on top of the Al electrode prior to the oxygen plasma exposure. During the oxidation Al and Hf interdiffuse resulting in a $HfO_x/AlO_x$ mixture. Figure 1(b) shows that in zero field the conductance has the required sharp maxima at the band-gap edge. However, in an applied field clear Zeeman splitting cannot be observed preventing precise extraction of $P$. From the model fit we can identify for this junction a positive polarization and deduce a spin-orbit scattering time $\tau_{so}$ of about 1 ps, which is roughly 40 times lower than what we obtain for the clean $Al/AlO_x$ case. Similar results are obtained when Ta is used instead of Hf.[18]

A high spin-orbit scattering rate induced in the superconductor by heavy atoms present at the Al/barrier interface is not an issue with MgO since the atomic number of Mg is low. The MgO junctions are obtained by depositing 20-Å Al bottom electrodes covered by a Mg film, deposited after removal of the shadow mask, with a thickness varied between 20 and 25 Å. Subsequently, the Mg film is exposed to an oxygen plasma with the same fixed parameters as used for the $AlO_x$ junctions, and finally Co or Fe top electrodes are deposited. The limited Mg thickness window of 20–25 Å is not arbitrary. Mg thicknesses less than 20 Å result in Al bottom electrodes with a high resistivity due to severe over-oxidation. Mg thicknesses larger than 25 Å cannot be used since for our oxidation parameters the oxidation of the Mg films is self-limited to 25 Å. During junction preparation, complications can arise due to possible intermixture of Al and Mg either during Mg deposition or the plasma oxidation. We have characterized the barrier structure of the MgO junctions with *in situ* angle-resolved x-ray photoelectron spectroscopy (XPS), and verified that at the MgO surface essentially no $AlO_x$ is present while at the Al/MgO interface an amount of $AlO_x$ is intermixed with MgO. This $AlO_x$ amount is largest in the MgO junctions prepared with 20 Å Mg thickness. The junction resistance-area product increases with $AlO_x$ amount from roughly $10^3$ k$\Omega$ $\mu$m$^2$ for the junctions prepared with 25-Å Mg films, to $10^5$ k$\Omega$ $\mu$m$^2$ with 20-Å Mg films. This is consistent with the higher barrier height for tunneling of $AlO_x$ as compared to MgO [2–3 eV versus 1 eV (Refs. 17 and 19)]. Thus, by varying the Mg film thickness, we vary the amount of $AlO_x$ intermixed with MgO at the Al/MgO interface, and the junction resistance varies over orders of magnitude accordingly.

The resistance increase of the MgO junctions during cooling is about 50%, which indicates that single-step tunneling is the dominant conduction mechanism. Figure 1(c) shows a representative conductance measurement of an Al/MgO/Fe junction. As for the $AlO_x$ junctions, high-quality superconducting gaps with sharp maxima at the band-gap edge are obtained, and the in-field measurement shows clear Zeeman splitting. From the model fits we extract a tunneling spin

TABLE I. Overview of results.

| Junction | $P$ |
|---|---|
| Al/$AlO_x$/Co | $+39\pm1\%$ |
| Al/$AlO_x$/Fe | $+41\pm1\%$ |
| Al/MgO/Co | $+30\pm2\%$ |
| Al/MgO/Fe | $+30\pm2\%$ |

polarization of $+30\pm2\%$ for both junctions with Fe and Co top electrodes. Interestingly, within the experimental accuracy, $P$ is independent of the $AlO_x$ amount and junction resistance. This means that the $AlO_x$ amount present at the Al/MgO interface has no significant influence on the tunneling polarization. In other words, *in our MgO junctions the junction resistance (barrier thickness and barrier height) appears to be at most weakly correlated with P, and instead the structure of the barrier/ferromagnet interface seems decisive*. This is consistent with earlier TMR experiments emphasizing on the crucial role of the atomic and electronic structure within several monolayers from the barrier/ferromagnet interface.[20–22]

Since the polarization of the density of states of the *s* electrons at the Fermi level in Co and Fe is positive, the positive sign of $P$ in the MgO junctions reflects that tunneling is dominated by *s* electrons, which is consistent with the absence of *d* orbitals in the barrier. The magnitude of $P$ obtained with the MgO junctions is significantly different as compared to the $AlO_x$ junctions (see Table I). This dependence can be brought about by the intrinsic electronic interface structure, but possibly also extrinsic effects can obscure the interpretation of our results. In the next paragraphs a more detailed analysis is used to exclude the most plausible extrinsic effects.

As mentioned by Monsma and Parkin,[23] one complication can be the oxidation of the ferromagnet at the barrier/ferromagnet interface. At low temperature, this oxide orders antiferromagnetically and prevents proper magnetization of the ferromagnet at the interface leading to a loss of tunneling spin polarization. This mechanism plays a role in magnetic tunnel junctions with antiferromagnetic barriers such as NiO and CoO where only relatively small TMR effects are obtained.[8] We have studied the oxidation state of the ferromagnet in our junctions with *in situ* XPS. For careful investigation of the interface, samples are used of which the thickness of the ferromagnetic electrode deposited on top of the barrier is only 4 Å. As an example of such an investigation, we consider here the case of Fe on MgO. Figure 2 shows the Fe $2p$ lines measured immediately after deposition (as-deposited) and, for comparison, after an exposure to oxygen. The absence of a chemical shift of about 5 eV, as observed in the deliberately oxidized spectrum, proves that there is no formation of $FeO_x$. In this way we have excluded oxidation of the ferromagnet in all our $AlO_x$ and MgO junctions (see also Ref. 24).

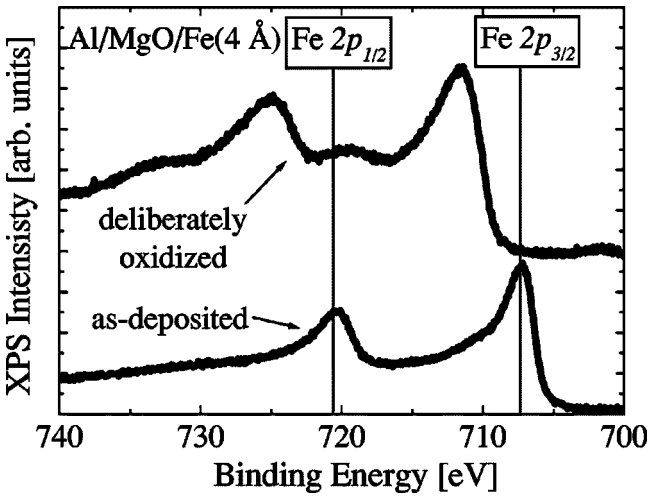


FIG. 2. *In situ* XPS (Al $K_\alpha$) measurements from which oxidation of Fe at the MgO/Fe interface can be excluded.

Another mechanism leading to loss of tunneling spin polarization is spin-orbit scattering at the barrier/ferromagnet interface due to the combination of spin-orbit interaction and a degree of disorder. This mechanism may explain the relatively small TMR effects obtained with the heavy metal oxides $TaO_x$ and $HfO_x$.[25,26] It cannot explain, however, why we have obtained a lower polarization with the MgO barrier since the atomic number of Mg is smaller than that of Al. Apparently, in our $AlO_x$ and MgO junctions spin-orbit scattering is not important. A third strong indication of the intrinsic nature of the barrier dependence is the fact that $P$ does not depend on the $AlO_x$ amount present at the Al/MgO interface, indicating a decisive role of the electronic structure at the MgO/ferromagnet interface. Concluding, we thus have substantiated our claim that the barrier dependence of $P$ is intrinsically determined by the MgO/ferromagnet interface. Conclusive evidence of the decisive role of the barrier for the character of the tunneling electrons would be the observation of a negative $P$ in, for example, Al/$SrTiO_3$/Co junctions.

Recently, measurements on epitaxial Fe/MgO/Fe junctions have shown large TMR effects,[27,28] from which a polarization can be estimated using the Julliere formula[29]

$$\mathrm{TMR}=\frac{2P^2}{1-P^2}. \tag{1}$$

This polarization, which we denote as the Julliere polarization, is roughly 50% to 60%. From calculated TMR magnitudes in epitaxial Fe/MgO/Fe junctions,[30,31] even higher values for the Julliere polarizations can be estimated. We point out that these Julliere polarizations cannot be compared directly with our polarization of 30%, since our MgO barrier is amorphous which certainly leads to a different electronic interface structure. Furthermore, in general, it is believed that the absence of the conservation of the momentum in parallel with the barrier during tunneling through amorphous barriers leads to an averaging of spin-polarized currents in different crystallographic orientations. This possibly reduces the effective tunneling spin polarization. A detailed theoretical understanding of $P$ in amorphous junctions which addresses this issue in full detail is currently not available.

In summary, by direct comparison between $AlO_x$ and MgO tunnel barriers and direct measurement of the tunneling spin polarization we have observed a barrier dependence which we claim is intrinsically determined by the electronic structure of the barrier/ferromagnet interface. With both Co and Fe as the ferromagnetic electrode, the tunneling spin polarization is roughly $+40\%$ in the $AlO_x$ junctions and $+30\%$ in the MgO junctions. This positive sign is consistent with the belief that in absence of *d* orbitals in the barrier material, tunneling is dominated by electrons with *s* character.

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