Negative Spin Polarization of Fe_3O_4 in Magnetite/Manganite-Based Junctions

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Epitaxial oxide trilayer junctions composed of magnetite (Fe_3O_4) and doped manganite ($La_{0.7}Sr_{0.3}MnO_3$) exhibit inverse magnetoresistance as large as -25% in fields of 4 kOe. The inverse magnetoresistance confirms the theoretically predicted negative spin polarization of Fe_3O_4. Transport through the barrier can be understood in terms of hopping transport through localized states that preserve electron spin information. The junction magnetoresistance versus temperature curve exhibits a peak around 60 K that is explained in terms of the paramagnetic to ferrimagnetic transition of the $CoCr_2O_4$ barrier.

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Highly spin polarized ferromagnetic materials have been the focus of recent fundamental and technological studies. In particular, the degree and sign of spin polarization of the carriers in these materials have been probed in a variety of spin polarized tunnel junctions. The spin polarization of the material is positive if the majority spin at the Fermi level is parallel to the bulk magnetization and negative if the minority spin at the Fermi level is parallel to the bulk magnetization. Negative spin polarization, however, has rarely been observed. Magnetite (Fe_3O_4) is unique in that it is predicted not only to have negative spin polarization but also to be a half-metallic ferromagnet with complete spin polarization at the Fermi level [1,2]. Experimentally, negative spin polarization has been observed in bulk Fe_3O_4 [3] and more recently Fe_3O_4 thin films [4,5] by spin-resolved photoemission studies. However, various transport measurements based on magnetic tunnel junctions have not been able to verify the negative spin polarization of the Fe_3O_4 films until recently [6].

Negative spin polarization has been observed in metallic $SrRuO_3$ based on Meservey-Tedrow–type spin polarized tunnel junctions [7]. De Teresa *et al.* have probed the spin polarization of transition metals such as Co, Fe, and $Ni_{0.8}Fe_{0.2}$ with a $SrTiO_3$ barrier and a $La_{0.7}Sr_{0.3}MnO_3$ counterelectrode and have found their spin polarization to be negative [8,9]. Magnetic tunnel junctions, where two ferromagnetic electrodes sandwich an insulating tunnel barrier, have been used to probe the spin polarization of Fe_3O_4. In such junctions, the junction magnetoresistance (JMR) (i.e., the difference in resistance values when the magnetization of the electrodes are parallel versus antiparallel) is related to the spin polarization and is maximized when the electrodes have complete spin polarization. Large JMR of up to 43% at 4.2 K has been reported by Seneor *et al.* in their glass/Co/Al_2O_3/iron oxide/Al structure in which the ultrathin polycrystalline iron oxide layer is composed of Fe_3O_4 and γ-Fe_2O_3 [10]. Various studies of epitaxial Fe_3O_4 magnetic tunnel junctions have yielded MR values only as high as 2% without verification of negative spin polarization [11,12]. Other epitaxial oxide junctions, made of doped manganites and CrO_2, have been fabricated with some success [13–15]. In magnetic tunnel junctions, the interface quality, tunnel barrier quality, surface/interface roughness, ferromagnetic electrode quality, magnetic domain walls, as well as the intrinsic behavior of ferromagnetic surfaces/interface greatly affect the JMR. The nature of magnetism at boundaries of spin polarized materials is a fundamental issue that has yet to be fully understood and may place technological limitations on the implementation and performance of spin polarized devices in memory applications.

We report the observation of negative spin polarization of Fe_3O_4 in epitaxial $Fe_3O_4/CoCr_2O_4$(CCO)/$La_{0.7}Sr_{0.3}MnO_3$(LSMO) magnetic trilayer junctions (MTJs). The inverse magnetoresistance, as high as -25% at 4 kOe, confirms the theoretically predicted negative spin polarization of Fe_3O_4. Transport through the paramagnetic insulating barrier can be understood in terms of hopping transport through localized states. This inelastic hopping process preserves electron spin information so that we observe a significant JMR in our junctions. Moreover, we observe a peak in the JMR as a function of temperature that we attribute to the paramagnetic to ferrimagnetic transition of the CCO barrier.

In our trilayer Fe_3O_4/CCO/LSMO junction, the bottom LSMO electrode, which exhibits colossal magnetoresistance (CMR) has been demonstrated to have a positive spin polarization up to 80% at low temperatures [16]. It is used as a spin analyzer to probe the spin polarization of the Fe_3O_4 film. In order to minimize the interface disorder between the Fe_3O_4 and the barrier, we have chosen a spinel structure barrier of CCO that has a 0.8% lattice mismatch with Fe_3O_4. Our previous studies of spinel ferrite thin films reveal that the existence of antiphase boundaries in films grown on MgO substrates deteriorates the magnetic properties of the spinel ferrites severely [17]. By introducing a CCO buffer layer on their $SrTiO_3$ (STO) and MgO substrates, Suzuki *et al.*

and Li *et al.* observed improved crystallinity and magnetic properties of ferrite films [11,18]. Therefore CCO is a better barrier than commonly used STO and MgO [12–14].

The trilayer of Fe_3O_4/CCO/LSMO is grown on (110) oriented STO substrates by pulsed laser deposition. The LSMO layer is grown at 700 °C, under 300 mTorr of O_2, then CCO is grown at 600 °C, under 7 mTorr of $1\%O_2/99\%N_2$ gas mixture, and finally the top electrode, Fe_3O_4, is grown under vacuum ($\sim 4 \times 10^{-6}$ Torr) at 400 °C. The typical thickness of the top and bottom electrodes is 800 and 600 Å, respectively, In this paper, all of the data are from junctions with a barrier thickness of about 60 Å and area ranging from 4 μm × 4 μm to 40 μm × 40 μm. The MTJs have been fabricated by conventional photolithography and an Ar ion mill. Despite the relatively large difference between the lattice parameters of Fe_3O_4 (a = 8.396 Å) and STO (a = 3.905 Å), the trilayer grows epitaxially on the STO substrate, as indicated by x-ray diffraction measurements. Ogale *et al.* have studied vertical transport in Fe_3O_4/STO/LSMO heterostructures grown on $LaAlO_3$ substrate and observed large MR values in high magnetic fields [19]. But they did not observe evidence in the MR data of parallel and antiparallel magnetization states of the ferromagnetic electrodes. Figure 1 is a typical hysteresis loop from an unpatterned trilayer structure measured at 80 K, with magnetic field applied along the in-plane [001] direction. The two coercive fields of 280 Oe and 1 kOe correspond to the LSMO and Fe_3O_4 layers, respectively. No exchange coupling exists between these two layer, thus ensuring free switching of the magnetization in the electrodes. The large coercivity difference in the two electrodes and squareness of the hysteresis loops create well-defined parallel and antiparallel states.

In this study, all transport measurements are carried out with current perpendicular to plane geometry and applied magnetic field parallel to the layers along the magnetically easy [001] direction. Nonlinear current-voltage (IV) characteristics have been observed. Field dependent transport measurements show characteristic JMR behavior as illustrated in Fig. 2. The fields, at which the junction resistance changes abruptly, correspond to the coercivities of the two electrodes. As a comparison, Fig. 1 is the M-H loop of an unpatterned trilayer sample measured at the same temperature. We have verified that the coercivity of Fe_3O_4 increases after patterning into micron size islands, while the coercivity of the bottom LSMO electrode with millimeter dimensions does not. This change in the coercivity of the Fe_3O_4 layer accounts for the difference of the switching fields observed in the MR curve of the junction and the M-H loop of the unpatterned sample. Since LSMO is majority spin polarized, the inverse MR (i.e., the junction resistance is higher in high magnetic field when the magnetizations of the two electrodes are parallel to each other) clearly indicates the negative spin polarization of the Fe_3O_4 electrode. In a field of 4 kOe and with JMR defined as $(R_{4kOe}\text{-}R_H)/R_{4kOe}$, the JMR values as high as -25% are observed in these junctions at 60 K. We observe a large background in the MR curves with a total JMR of -33% at 7 tesla. This background cannot be attributed to the misalignment of the field with respect to the easy in-plane direction of the junction but may be a manifestation of the high fields necessary to align the LSMO and Fe_3O_4 with the applied magnetic field [20,21]. Typical junction resistances are several kΩ at room temperature and increase monotonically with decreasing temperature. A straightforward calculation of the resistance of the electrodes is more than 2 orders of magnitude smaller than the junction resistance, thus ensuring a uniform current distribution through the junction area.

The temperature dependence of the JMR is shown in Fig. 3 (open circles). At room temperature, we observe a well-defined JMR of -0.5% at 4 kOe. The JMR increases

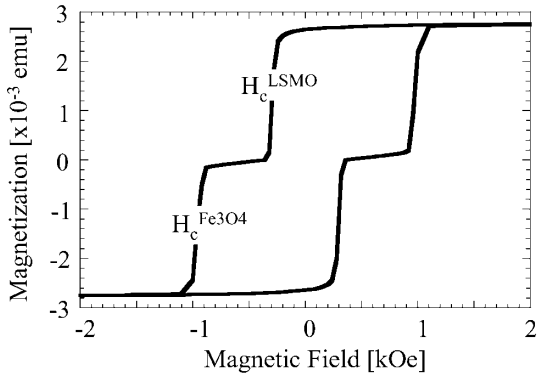

FIG. 1. Magnetization vs magnetic field loop from an unpatterned Fe_3O_4/CCO/LSMO trilayer structure at 80 K, with magnetic field applied along the in-plane [001] direction.

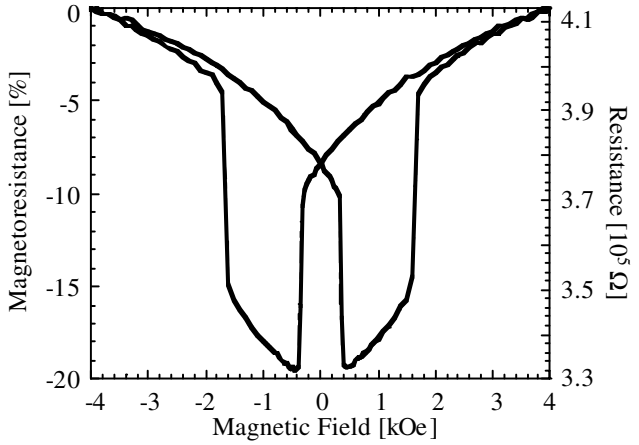

FIG. 2. Junction magnetoresistance vs magnetic field at 80 K for a 20 μm × 20 μm area junction.

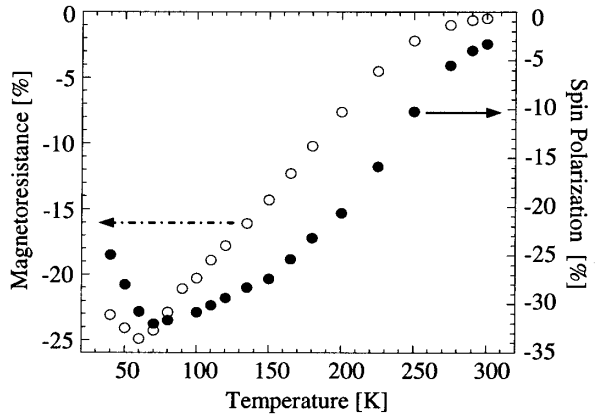

FIG. 3. Junction magnetoresistance (open circles) and deduced spin polarization of Fe_3O_4 (solid circles) as a function of temperature, with JMR defined as $(R_{4kOe}\text{-}R_H)/R_{4kOe}$.

with decreasing temperature but exhibits a peak around 60 K. This temperature dependence contrasts with the monotonic temperature dependence seen in epitaxial CMR sandwich tunnel junctions [13,14]. In addition, JMRs of CMR/oxide/CMR junction disappear by 270 K [14]. However, the fact that we observe JMR in our Fe_3O_4/CCO/LSMO junctions at 300 K indicates that the vanishing JMR in CMR sandwich tunnel junctions is not due to the vanishing spin polarization of CMR.

Using temperature dependent spin polarization data of LSMO, for example, from Noh *et al.* [14], we estimate the temperature dependent spin polarization of Fe_3O_4 from Jullière's model [$P_{Fe3O4} = MR/(2 + MR)P_{LSMO}$] [22], as shown in Fig. 3 (solid circles). While Jullière's model is too simplistic for our junctions, it still does provide an estimate. For temperatures greater than 100 K, we fit the spin polarization to $P(T) = P_0(1 - \alpha T^{3/2})$ which is ascribed to magnon assisted scattering [23]. From this analysis, we obtain a spin polarization value of $P_0 = -39\%$, which qualitatively agrees with bulk spin polarized photoemission studies at low temperatures [3]. However, in our junction, the spin polarization of Fe_3O_4 films decreases faster with increasing temperature than what is observed in bulk studies. Spin polarization as high as -80% has been reported recently in spin-resolved photoemission studies of Fe_3O_4 thin films [4]. However, a theoretical calculation conducted by Srintitiwarawong and Gehring suggests that, in a tunnel device, the spin polarization of the Fe_3O_4 film is limited to 67% even at 0 K, because of surface effects and the quantum mechanical coupling and relaxation of the conduction electron and core spin [24].

In our junctions, the CCO barrier, which is a weak paramagnet above 95 K, is 60 Å thick. Our barrier thicknesses are too thick for direct tunneling. In fact, a fit of our *IV* characteristics to the Simmons model [25], for applied biases less than the barrier height, does not predict reasonable parameters for the barrier height (~ 1.0 eV) and thickness (20 Å). A more appropriate mechanism is hopping transport through a number N of localized states [26]. *IV* characteristics of the junction fit well to hopping through $N = 2$ localized states at low bias and $N = 2$ and $N = 3$ localized states at higher bias as shown in Fig. 4. The bias dependence of JMR clearly indicates that the dominant contribution to the JMR is inelastic hopping over the whole temperature range. The localized states may be attributed to oxygen defects or cation disorder. Since, in previous studies, we have found Cr^{3+} has a strong preference for the octahedral site in the spinel structure to the extent of displacing Co^{2+} from octahedral to tetrahedral sites [27], cation disorder should be minimal in CCO. Annealing experiments of insulating spinel structure ferrites in air at 1000 °C indicate that oxygen can easily diffuse in and out of the open spinel crystal structure with an accompanying change in the electronic properties. Therefore, the localized states are likely to be nonmagnetic oxygen defects that are not associated with spin-flip scattering and therefore do not suppress JMR. Thus, the observed JMR can be explained in terms of the inelastic hopping of electrons through the CCO barrier via scattering events that preserve spin information.

A closer look at the JMR as a function of temperature reveals a peak around 60 K. The decrease in JMR as a function of temperature $T > 100$ K can be attributed to the temperature dependence of a spin wave related reduction of the spin polarization as well as the temperature dependence of a spin independent conductance, in our case inelastic hopping, in the barrier. Below 60 K, the JMR is suppressed. We believe this suppression is closely

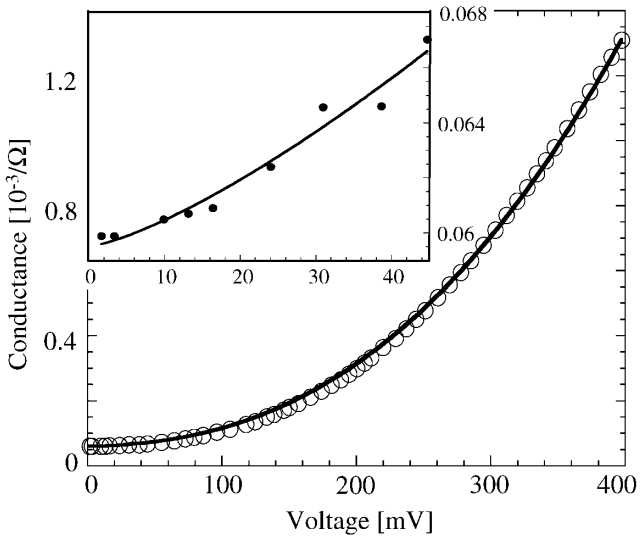

FIG. 4. Junction conductance ($G = I/V$) as a function of bias voltage. The circles are measured data. In the inset, junction conductance is fitted to hopping through $N = 2$ states ($G = G_0 + \sum_N G_N^{hop}[V]^{N-[2/(N+1)]}$). At higher bias, the data is fitted to hopping through $N = 2$ and $N = 3$ localized states [26].

related to the paramagnetic to ferrimagnetic transition in the CCO barrier and not to the Verwey transition ($T_V = 120$ K) which is broadened significantly in our Fe_3O_4 layer. Although bulk CCO and our thick (~ 1000 Å) CCO films show a Curie temperature at 95 K, for a layer as thin as 60 Å, the T_C is most likely suppressed to lower temperature. As CCO becomes ferrimagnetic, the magnetic state of the electrodes and barrier may be considered in the following way. Because the Fe_3O_4 and CCO are isostructural, we expect strong exchange coupling between these layers. We have found that spinel ferrite bilayers are strongly exchange coupled to each other, due to their structural similarity [28]. In fact, we observe an exchange coupling across the interface that is as strong as that observed within the thin film layers, but no exchange coupling between a cubic perovskite manganite ferromagnet and ferrimagnetic spinel. In this case, we believe that there is strong exchange coupling between Fe_3O_4 and CCO below the T_C of CCO. In addition, the magnetic transition induces an exchange splitting of the CCO barrier so that electron spin parallel to the overall magnetization of the CCO sees a lower barrier height and electron spins antiparallel to the overall magnetization of CCO see a higher barrier height. Thus, compared to the case where CCO is paramagnetic, the difference of the junction resistance between the two states decreases and so does the JMR value. To within the accuracy of our measurement of the barrier thickness, the observed reduction of the JMR as a function of increasing barrier thickness from 60–80 Å is consistent with our model. Therefore, the peak in the JMR as a function of temperature is a competition between the spin wave related reduction in spin polarization with increasing temperature and a reduction in JMR associated with the ferrimagnetic transition of the barrier with decreasing temperature.

In conclusion, we have successfully demonstrated negative spin polarization of Fe_3O_4 in Fe_3O_4/LSMO based magnetic trilayer junctions. Spin-dependent transport behaviors have been observed, with a JMR value as high as -25% and -33% in fields of 4 kOe and 7 tesla, respectively. The observed inverse magnetoresistance confirms the theoretically predicted negative spin polarization of Fe_3O_4. With the measured MR value from the tunnel junctions and spin polarization data of the LSMO electrode, we have deduced the spin polarization of Fe_3O_4 to be -39%. Transport through the paramagnetic insulating barrier can be understood in terms of hopping transport through localized states that preserve spin information.

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