Voltage and temperature dependence of the grain boundary tunneling magnetoresistance in manganites

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Abstract.

We have performed a systematic analysis of the voltage and temperature dependence of the tunneling magnetoresistance (TMR) of grain boundaries (GB) in the manganites. We find a strong decrease of the TMR with increasing voltage and temperature. The decrease of the TMR with increasing voltage scales with an increase of the inelastic tunneling current due to multi-step inelastic tunneling via localized defect states in the tunneling barrier. This behavior can be described within a three-current model for magnetic tunnel junctions that extends the two-current Jullière model by adding an inelastic, spin-independent tunneling contribution. Our analysis gives strong evidence that the observed drastic decrease of the GB-TMR in manganites is caused by an imperfect tunneling barrier.

The tunneling resistance between two ferromagnetic metal layers separated by a thin insulating barrier depends on the relative orientation of the magnetization and the electron spin polarization in each layer \[ R = (R_{\uparrow\uparrow} - R_{\uparrow\downarrow})/R_{\uparrow\uparrow} \]. Since for materials with large spin polarization a large tunneling magnetoresistance (TMR) can be achieved, magnetic tunnel junctions have recently attracted much attention and their use in memory devices in envisaged. Due to their half-metallic ferromagnetic state with only a single spin band crossing the Fermi level, the spin polarization of the perovskite manganites of composition \( \text{La}_{2/3}D_{1/3}\text{MnO}_3 \) with \( D = \text{Ca}, \text{Sr}, \text{and Ba} \) is close to 100%. According to the Jullière model, a high TMR ratio \( \Delta R/R = (R_{\uparrow\uparrow} - R_{\uparrow\downarrow})/R_{\uparrow\uparrow} \) is expected making these materials attractive for magnetic tunnel junctions. Here, \( R_{\uparrow\uparrow} \) and \( R_{\uparrow\downarrow} \) is the tunneling resistance for parallel and anti-parallel magnetization orientation and \( P \) is the spin polarization where \( a \) is the fraction of majority spin electrons in the density of states of layer \( i \). Indeed a high TMR ratio well above 100% has been achieved at low temperatures and low applied fields \( H \) of the order of 10 mT. In addition to planar type tunnel junctions, a large low field magnetoresistance was found for grain boundaries (GBs) in the perovskite manganites...
In contrast to the colossal magnetoresistance (CMR) observed in single crystals, the GB magnetoresistance can be observed at low $H \sim 10 \text{ mT}$ and over the entire temperature range below the Curie temperature $T_C$. The GB magnetoresistance is attributed to spin-polarized tunneling across an insulating GB barrier between two ferromagnetic grains. For both planar junctions and grain boundary junctions (GBJs) based on the manganites a large TMR has been observed only at low temperatures and junction voltages, which strongly decreases with increasing temperature and bias voltage. The origin of this effect has not been clarified so far. A similar but somewhat weaker decrease of the TMR also has been found for magnetic tunnel junctions employing Al$_2$O$_3$ barriers and Co and Permalloy electrodes as well as for granular and powder systems. Also for the latter systems the origin of the voltage and temperature dependence of the TMR is discussed controversially.

In this Letter we report on the systematic study of the GB magnetoresistance in La$_{2/3}$Ca$_{1/3}$MnO$_3$ (LCMO) as a function of voltage $V$ and temperature $T$ using well-defined single GBJs. By analyzing the current-voltage characteristics (IVCs) in terms of the Glazman-Matveev (GM) theory for multi-step tunneling we show that with increasing $V$ inelastic tunneling contributes more and more to the charge transport across the GB barrier. Since spin polarization may be not conserved in the inelastic channel, the inelastic tunneling current does not contribute to the magnetoresistance and the measured TMR ratio is reduced accordingly. In the presence of the inelastic channel, the well-known two-current model of Julli`ere, which assumes that the two spin species of electrons tunnel elastically, has to be extended to a three-current model to account for the inelastic, spin-independent tunneling current. Within such three-current model the TMR ratio $\Delta R/R$ is shown to be proportional to the ratio $I_e/(I_e + I'_e)$ of the elastic tunneling current, $I_e$, and the sum of the elastic and inelastic tunneling current, $(I_e + I'_e)$ as discussed in detail below. Such proportionality has been found in our experiments on LCMO-GBJs.

The LCMO-GBJs were fabricated by pulsed laser deposition of epitaxial, 20 to 100 nm thick LCMO films on symmetrical, [001] tilt SrTiO$_3$ bicrystals with a misorientation angle of 24°. After film deposition the samples were annealed at 950°C in oxygen atmosphere for one hour. X-ray analysis of the films showed only (00l) reflexes and the FWHM of the (002) rocking curve before annealing typically was $\leq 0.03^\circ$. After the annealing process the FWHM slightly increased but stayed below $0.1^\circ$. Microbridges of 10 to 30 µm width straddling the GB were patterned using optical lithography and Ar ion beam etching. In this way well defined individual GBJs are obtained. For comparison we also fabricated microbridges of exactly the same size that do not cross the GB as shown in the inset of Fig. 1. These microbridges without GB are used for the analysis of the film properties. They also are used to determine the additional voltage drop along the film adjacent to the GB. This voltage drop can then be subtracted from the total voltage measured for an identical microbridge with GB to get the voltage drop across the GB alone. In the same way, the small series resistance due to the film can be determined and subtracted from the measured total resistance to obtain the pure GB resistance and TMR ratio. Further details on the transport properties and the microstructure of the GBJs have been reported recently.

Typical resistance vs temperature, $R(T)$, curves of a LCMO film are shown in Fig. 1. The maximum in the $R(T)$ curve that can be associated with $T_C$ is about 225 K and is shifted to 275 K at 8 T. Comparing the $R(T)$ curves of microbridges of the same size but with and without GB, the resistance of those containing a single GB is found to be enhanced considerably below $T_C$ as has been discussed in detail elsewhere. Below about 160 K the resistance of bridges with GB is dominated by the GB resistance. The appearance of an additional GB resistance below $T_C$ that becomes dominant at $T \ll T_C$ recently has been discussed in terms
Fig. 1. – Resistance vs. temperature of a 80 nm thick La$_{2/3}$Ca$_{1/3}$MnO$_{3-\delta}$ thin film with (dashed lines) and without (solid lines) grain boundary at zero field and at 8 T. All curves were measured at a bias voltage of $V = 10$ mV. The inset shows a sketch of the sample configuration.

of the formation of a depletion layer at a disordered, paramagnetic GB interface resulting in a tunneling barrier [10, 11].

Fig. 2. – Current-voltage characteristics of a 24° [001] tilt GBJ in a 80 nm thick La$_{2/3}$Ca$_{1/3}$MnO$_{3-\delta}$ film. The dashed lines are fits to the Glazman-Matveev model. The inset shows the IVC for $T = 40$ K on a log-log scale.

In Fig. 2 typical IVCs of a LCMO-GBJ are shown between 4 and 160 K. In order to get the pure characteristics of the GB we have corrected the measured data by subtracting the additional series resistance of the film adjacent to the GB. The film resistance, which is smaller
than about 30% of the GB resistance for $4 \leq T \leq 160$ K, has been determined from an identical microbridge without GB on the same substrate. Whereas the IVCs of microbridges without GB are ohmic, highly non-linear IVCs are found for the microbridges containing a GB with the non-linearity increasing with decreasing $T$. We also note, that linear IVCs are found for $T \geq T_C$. It has been shown by Klein et al.\cite{10, 11} that the non-linear IVCs of bicrystal GBJs in the manganites can be well fitted by the GM-theory\cite{18}. In this theory, in addition to the elastic tunneling channels multi-step tunneling via a number of $n$ localized states within the tunneling barrier is taken into account. Within the GM-model the conductivity $G(V,T)$ is given by

$$G(V,T) = G_0 + \sum_{n=1}^{\infty} G_n(V,T),$$

where the conductance $G_0$ represents the direct tunneling term and $G_n$ the tunneling via $n \geq 1$ localized states. For $eV < k_B T$ and $eV \gg k_B T$, $G_n(V,T)$ can be expressed as

$$G_n(V) = a_n \cdot V^{(n - \frac{1}{2})} \text{ for } eV \gg k_B T$$

$$G_n(T) = b_n \cdot T^{(n - \frac{1}{2})} \text{ for } eV \ll k_B T,$$

where $a_n$, $b_n \propto \exp(-2d/(n+1)\alpha)$ are constants depending on the radius $\alpha$ of the localized states, their density and the barrier thickness $d$. We note that these expressions are valid as long as $eV$ and $k_B T$ are small compared to the barrier height. That is, with a barrier height of the order of 1 eV\cite{10, 11}, the GM-expressions can be used over the entire $T$ range of our experiments and for voltages up to about 100 mV. We note that $eV \gg k_B T$ for most part of the measured IVCs at $T \leq 160$ K. Then, the IVCs can be fitted by

$$I = G_0 V + a_1 V + a_2 V^{\frac{3}{2}} + a_3 V^2 + \cdots.$$  

According to the GM-theory, direct tunneling and tunneling via a single localized state ($n = 1$) gives the elastic tunneling current $I^e$, whereas the $n \geq 2$ channels yield the inelastic tunneling current $I^i$. Fitting the IVCs at different $T$ to the GM-theory we can derive the ratio $I^e/(I^e + I^i)$ as a function of $V$ and $T$. As demonstrated by Fig. 2, the experimental data can be well fitted by the GM-expressions at all $T$ up to $V \approx 0.15$ V. For all samples the coefficients $a_i$ with $i \geq 4$ were negligible, i.e. only inelastic channels up to $n = 3$ are required to fit the data. The fits cover more than three orders of magnitude on the current and voltage axis as shown in the inset of Fig. 2. This gives strong evidence that the non-linear IVCs are caused by inelastic tunneling processes which increase with increasing $V$. We note that not all samples could be fitted as perfect as shown in Fig. 2. However, the deviations from the GM-model always were small and fits to other models, e.g. the Simmons model\cite{20} gave much worse results. Deviations from the GM-theory are expected in the presence of additional inelastic effects such as the excitation of surface magnons\cite{21} that are not included in GM theory.

We now discuss the expected interdependence between the ratio $I^e/(I^e + I^i)$ and the measured TMR ratio $\Delta R/R$. To take into account the inelastic tunneling current we use a three-current model that extends the well known two-current Julli`ere model\cite{1} by adding inelastic tunneling channels. In the following we assume that the inelastic tunneling current depends on $V$ and $T$ but is the same for the parallel and anti-parallel magnetization arrangement, i.e $I_{ap}^i = I_{ap}^i = I^i$. This is in contrast to the $V$ and $T$ independent elastic tunneling current which, however, is spin-dependent resulting in $I_{ap}^e < I_{ap}^e$. The assumption that $I^i$ does not depend on the relative magnetization orientation is justified, since spin orientation is expected to be not conserved in an inelastic tunneling process. With this assumption the
three-current model yields

$$\frac{\Delta R}{R}(V, T) = \frac{I_{ap}}{I_{ap} + I^i(V, T)} \left( \frac{I_e}{I_{ap}} - 1 \right). \quad (5)$$

It can further be shown that the expression in brackets is given by the $V$ independent TMR ratio of the Jullière model resulting in

$$\frac{\Delta R}{R}(V, T) = \frac{I_{ap}}{I_{ap} + I^i(V, T)} \left( \frac{\Delta R}{R} \right)_{Jullière}(T). \quad (6)$$

That is, the TMR ratio $\frac{\Delta R}{R}(V)$ measured at constant temperature is expected to be proportional to $\frac{I_{ap}}{I_{ap} + I^i(T)}(V)$. In order to check such possible proportionality we have measured the TMR ratio as a function of $V$ for different $T$. The ratio $\frac{I_{ap}}{I_{ap} + I^i(T)}(V)$ has been determined independently from the zero field IVCs measured at constant $T$ as discussed above.

![Graph](image_url)

Fig. 3. – $R(0) - R(H)/R(H)$ measured at different bias voltage plotted versus the applied magnetic field at 4 K for a $24^\circ [001]$ tilt LCMO-GBJ. The arrow indicates the direction of the field sweep. The field is applied within the film plane parallel to the current.

In Fig. 3, we have plotted $[R(0) - R(H)]/R(H)$ versus the applied magnetic field measured at different bias voltages. For the bias voltage only the voltage drop across the GB is used. In order to determine the TMR ratio, for $R_{\uparrow \downarrow}$ the maximum of the $R(H)$ curve was used which is slightly shifted away from $H = 0$ due to the finite coercivity field resulting in hysteretic $R(H)$ curves. For clarity, in Fig. 3 we only have plotted the data for one sweep direction, i.e. the hysteretic behavior upon field reversal is not shown. Fig. 3 shows that the TMR ratio of the GBJ is drastically reduced with increasing bias voltage. This effect is clearly found for $4 K \leq T \leq 120 K$, where the GB resistance dominates and non-ohmic IVCs are observed[22].

In order to further analyze the data, in Fig. 4 we plotted $\frac{\Delta R}{R}$ for $\mu_0 H = 1.5 T$ together with $\frac{I_{ap}}{I_{ap} + I^i(T)} \left( \frac{\Delta R}{R} \right)_{Jullière}$ versus the applied bias voltage. Here, the ratio $\frac{I_{ap}}{I_{ap} + I^i(T)}$ has been determined from the measured zero field IVCs using the GM-model as described above and
Fig. 4. $\Delta R/R$ (symbols) at $H = 1.5$ T plotted versus bias voltage and temperature for a 24° [001] tilt LCMO-GBJ. The lines show $\frac{i_{ep}}{i_{ep} + i_{i}} \left( \frac{\Delta R}{R} \right)_{\text{Jullière}} (T)$. 

$\left( \frac{\Delta R}{R} \right)_{\text{Jullière}} (T)$ is chosen to give the optimum fit to the measured $\Delta R/R$ data. Fig. 4 demonstrates that there is good coincidence between the two quantities as expected according to the three-current model. This strongly suggests that the observed decrease of the TMR ratio of the LCMO-GBJs is due to inelastic tunneling processes across a GB barrier containing a high density of localized defect states. 

Fig. 4 shows that for $\Delta R/R$ a maximum value of about 300% is obtained at low $T$ and $V$. Formally, this corresponds to a spin polarization of about 80%. We note, however, that the actual spin polarization in LCMO may be slightly larger and the derived value of 80% only represents a lower estimate, since we do not know the detailed domain structure in the LCMO film. Fig. 4 clearly shows that the TMR ratio strongly decreases with increasing $V$. This behavior is well described within the three-current model discussed above due to an increase of the inelastic tunneling current with increasing $V$. The three-current model provides an intuitive description of the magnetotransport suggesting that for the manganite GBJs there is a significant inelastic tunneling current mediated by multi-step tunneling via localized defect states within the GB barrier. That is, the strong reduction of the GB magnetoresistance with increasing $T$ and $V$ is caused by an imperfect tunneling barrier containing a large density of localized defect states. For the LCMO-GBJs this most likely is related to disorder, strain and oxygen non-stoichiometry at the GB. Evidently, a considerable improvement of the TMR ratio is possible by reducing the density of defect states in the tunneling barrier. To what extent other inelastic processes such as the excitation of surface magnons play a role cannot be derived from our present data and has to be further evaluated. We finally note that similar results have been obtained for La$_{2/3}$Sr$_{1/3}$MnO$_3$-GBJs and other misorientation angles showing that the observed behavior seems to be general for GBJs in the doped manganites.

In the three-current model the inelastic tunneling channel provides an additional transport channel that does not depend on the relative orientation of the magnetization. That is, this inelastic channel acts as a parallel shunt for the resistance representing the elastic, spin polarization conserving channel. It is obvious that this results in a reduction of the TMR ratio. We note that this situation in ferromagnetic LCMO-GBJs is analogous to that in
superconducting cuprate GBJs. For the latter, phase coherence is lost in the inelastic channels and therefore Cooper pairs cannot be transferred via these channels in the same way as spin polarized electrons in magnetic tunnel junctions. For superconducting tunnel junctions the resistive shunt due to the additional inelastic channel results in a reduction of the characteristic junction voltage equivalent to the reduction of the TMR ratio in magnetic junctions. Recently, Gross et al.\cite{10, 11} proposed the Intrinsically Shunted Junction model to explain the effect of inelastic tunneling on the properties of GBJs in the cuprate superconductors.

In summary, we have performed a systematic analysis of the $V$ and $T$ dependence of the low field TMR of LCMO-GBJs. We found a strong decrease of $\Delta R/R$ with increasing $V$ and $T$. As key result we found that $\Delta R/R$ is proportional to $I^e/(I^e + I^i)$. This gives strong evidence that the reduction of the TMR ratio is caused by an increase of $I^i$. We have used a three-current model that extends the well known two-current Jullière model by adding an additional inelastic tunneling contribution. This model naturally explains the observed proportionality and astonishingly well describes the $V$ dependence of the measured TMR ratio. Our results suggest that the drastic decrease of the GB-TMR in manganites is caused by an imperfect tunneling barrier and can be at least partly avoided by improving the barrier quality. We finally note that the three-current model should be applicable to other magnetic tunnel junctions or granular systems where imperfect barriers also may be the origin of a considerable $V$ and $T$ dependence of the TMR.

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