PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Towards control of the switching field: manganite permalloy heterostructures

By M. R. J. Gibbs[1], M. Ziese[1], G. A. Gehring[1], H. J. Blythe[1], D. J. Coombes[1], S. P. Sena[1] and C. Shearwood[2]

[1]*Sheffield Centre for Advanced Magnetic Materials and Devices, Department of Physics, University of Sheffield, Sheffield S3 7RH, UK*

[2]*Sheffield Microelectromechanical Systems Unit, Department of Electronic and Electrical Engineering, University of Sheffield, Sheffield S1 3JD, UK*

It is well established that the resistance of manganites is a function of magnetization. In a conventional experiment, the magnetization is changed by the application of a magnetic field, and a resistance change is measured. The manganites show two different forms of colossal magnetoresistance: that which is associated with very narrow domain walls in polycrystalline samples with grain boundaries, and that associated with magnetic ordering near to the transition temperature. Although the former only requires low fields, it is also only observed at low temperatures. Hence there is a real need to reduce the magnetic field required to observe the effect near to the transition where, currently, fields of the order of 1 T are required. An alternative approach is to change the state of magnetization by injection of spin-polarized carriers. We have recently taken out a patent which describes a general technique which may be used to inject carriers: a manganite permalloy heterostructure. This paper discusses the background to this approach in terms of the band structures of permalloy and manganite, and the way in which the switching field may be reduced. We present results from our experimental programme, which is attempting to realize a structure in current perpendicular to plane geometry to study spin injection.

Keywords: colossal magnetoresistance; heterostructures; device; LaCaMnO

1. Introduction

The study of colossal magnetoresistance (CMR), was stimulated by the work of von Helmolt *et al*. (1993) on thin films. The subject has also recently been reviewed by Ramirez (1997). CMR materials are perovskite structures; the parent compound being the manganite $LaMnO_3$. Substitution of La in $LaXMnO_3$ by X = Ca, Ba or Sr gives hole doping, and the magnetic phase transition temperature, T_C, rises to around room temperature. While the maximum resistivity changes observed are orders of magnitude greater than anything seen in conventional magnetoresistance (e.g. in NiFe), very large, often tesla, fields are required. There is a narrow field range, around the coercive field, where the differential response is high, but bias fields of the order of 5 mT are required. This is a substantial field to achieve from local bias magnets. The physics of these materials is deserving of study in its own right, but if significant differential response at low applied field can be achieved, then application in such areas as magnetic recording heads and magnetic field sensors may become possible.

We shall adopt the following definition of the magnetoresistance ratio $M_r(H)$ following Ramirez (1997), whereby

$$M_r(H) = \frac{\rho(0) - \rho(H)}{\rho(H)}, \tag{1.1}$$

where $\rho(0)$ is the resistivity measured in zero applied field, and $\rho(H)$ that measured in an applied field H. This ratio has been typically reported as equal to 0.8 in $La_{0.75}Ca_{0.25}MnO_3$ (Schiffer *et al.* 1995) for an applied field of 4 T (i.e. $M_r(4) = 0.8$).

Attempts have been made to investigate ways of reducing the necessary bias field. Hwang *et al.* (1996*a*) placed ($(Mn,Zn)Fe_3O_4$) magnets at either end of a sample of $La_{0.67}Y_{0.07}Ca_{0.33}MnO_3$. The Mn–Zn ferrite acts a soft magnetic material, and concentrates flux into the manganite. The applied field is thus essentially magnified by the effective permeability of the ferrite. It is assumed that there is good flux linkage between the ferrite rods through the manganite. Given that shape anisotropy will dominate the permeability of the ferrite, this route is not attractive for devices requiring small physical size such as read-heads in magnetic recording.

It has also been observed that, at low temperatures, there is a significant contribution to the magnetoresistance from grain boundaries. $M_r(0.5) = 0.25$ at 25 K has been found in $La_{0.67}(Ca,Sr)_{0.33}MnO_{3-\delta}$ when the sample has a grain size of 3 μm (Gupta *et al.* 1996). Careful comparison of epitaxial (grain boundary free) and polycrystalline (often μm-sized grains) has demonstrated that the phenomenon is to be associated with spin-polarized transport across the grain boundaries. Using a trilayer structure of $La_{0.67}Sr_{0.33}MnO_3$–$SrTiO_3$–$La_{0.67}Sr_{0.33}MnO_3$, $M_r(0.01) \approx 0.83$ at 4.2 K has been reported (Sun *et al.* 1996). While this result was gained at low temperature, Mathur *et al.* (1997) and Steenbeck *et al.* (1997) have investigated the properties of transport across a single grain boundary. The low-field MR close to the ferromagnetic–paramagnetic boundary is greater than that observed by Hwang *et al.* (1996*b*) in polycrystalline material, and demonstrates one feasible route for room temperature applications. We now proceed to describe the physics of a new approach for gaining significant MR at low fields and at room temperature.

2. Basic physics of the heterostructure

We propose to try to reduce the magnetic field required to give CMR by growing $LaXMnO_3$ with a soft, adjacent layer (SAL). The aim is to use polarized spin injection from the SAL to create a change of magnetization in the $LaXMnO_3$, rather than an external field. The SAL may have a switching field comparable with that in the best soft ferromagnetic films, perhaps as low as 20 A m^{-1}.

The ferromagnetism of the manganite is produced because the manganite is a half-metallic ferromagnet (Pickett & Singh 1996). This means that all the conduction electrons are polarized parallel to the magnetic moment, or put another way, the Fermi level lies in the band for the majority spin electrons and in the gap for the minority electrons; hence the material is metallic for one electron spin and insulating for the other. Let us consider the interface between manganite and a strong ferromagnet such as nickel (in such a material there are no empty d-states at the Fermi level for one spin band, but the Fermi level passes through the other spin band; in this case of course there are conduction electron states of both spins present at the Fermi level). A schematic density of states of d-electrons is shown in figure 1, and is

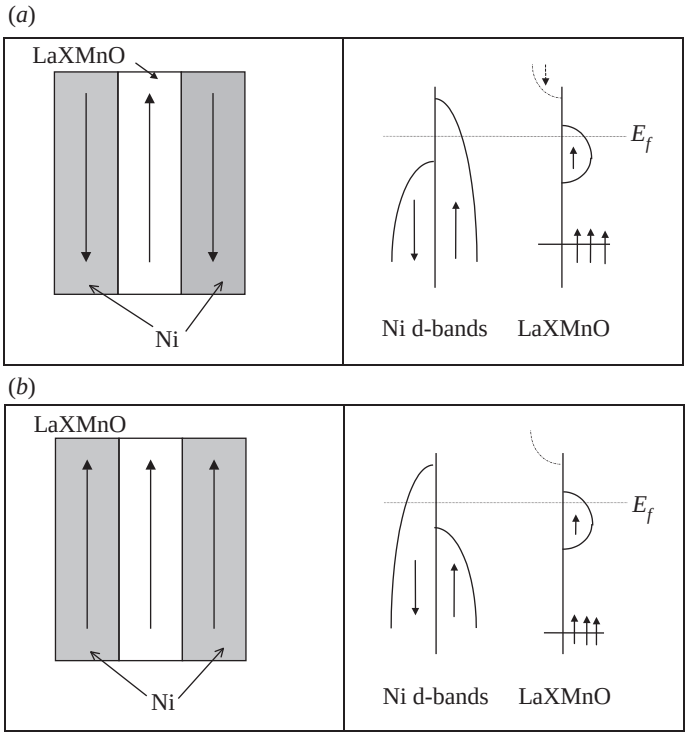

Figure 1. A schematic representation of the macroscopic magnetization (left) and densities of states for d-electrons (right) of LaXMnO and a soft adjacent strong ferromagnet. (*a*) Antiparallel and (*b*) parallel magnetization between the SAL and the LaXMnO.

similar to that shown by Hwang *et al.* (1996*b*). Consider an interface in which the magnetization of the two materials is antiparallel (figure 1*a*). In this case, the Ni d-electrons can delocalize into the manganite. This process is not possible if the two magnetizations are parallel (figure 1*b*). By the uncertainty principle, the energies of the less localized states are lowered and so the antiparallel configuration is favoured. The amount of energy lowering can be related to the exchange (Coombes & Gehring 1998).

Hence one of the ways in which the presence of the Ni (SAL) affects the manganite is by producing a local ordering field. The magnetization in the manganite will respond as

$$M(x,y,z) = b_0 \iint \mathrm{d}x'\mathrm{d}y'\chi(x-x',y-y',z), \tag{2.1}$$

where b_0 is the effective field on the surface layer given by $J_\mathrm{s}/g\mu_\mathrm{B}$, with J_s the exchange integral, g the Lande factor and μ_B the Bohr magneton. This effect will be largest when the susceptibility, χ, is large, i.e. close to T_C.

There are other effects. The phase diagram of the manganites as a function of doping shows that the value of T_C is a strong function of the electron doping. This arises because the superexchange which occurs when the sample is insulating competes with the double-exchange which is allowed when the electrons are conducting. The phase diagram was calculated within a mean-field theory long ago (Kubo &

Ohata 1972). There will be a change in the electron concentration close to the interface which will cause a local change in T_C and hence a change in the local ordering. However, this may be a very small effect. When we include the fact that the electrons which will be involved in the screening of the barrier will be polarized, we see the presence of the SAL can actually affect the mechanism of ferromagnetic ordering in the LaXMnO, and induce magnetism of a well-defined polarity. In the absence of this, the LaXMnO would have been on the paramagnetic or spiral side of the metal–insulator–phase transition. These effects have been calculated (Coombes & Gehring 1998).

There is a third effect which arises because of the interface resistance. This would be seen below the transition temperature where the manganite coercive field would prevent it following the magnetism of the permalloy as it switched in a low field. This would mean that as one traversed a hysteresis loop it would be possible to see the change in the boundary resistance as the manganite and the permalloy were switched parallel to antiparallel. In the permalloy the total current is carried predominantly by the minority d-electrons; this is because they are less scattered by the high density of states at the Fermi level. In the manganite, assuming total spin polarization the current is carried 100% by the majority of electrons because there are no minority states at all at the Fermi surface. However, the d-electrons will have bigger hybridizing matrix elements across the boundary because there are only d-electrons on the manganite side. The effect of the interface term would be enhanced if a gold layer were interposed between the permalloy and the manganite because this would have the effect of reducing the exchange interaction very strongly. With the gold layer in place it would be easier to have the manganite and the permalloy magnetized antiparallel because they would then be essentially decoupled.

This paper explains the ways in which we have begun to address the relative importance of the three mechanisms described here and to exploit them in a device. The device has been the subject of a patent filed by the University of Sheffield (Gibbs *et al*. 1998).

3. Issues to be addressed

We may consider these effects separately. First, we consider the effect of the Ni on changing both the magnetization due to the exchange field and the electron concentration, which also changes T_C and hence causes a change in the magnetization profile near the interface. This effect will be large when the bulk susceptibility is also large, i.e. close to the ordering temperature T_C. The second effect depends upon the change in the interface resistance, and will be large when there is a very large degree of spin polarization in the manganite, i.e. at low temperatures. The experiments described below have been done in a regime in which the first effect will be likely to dominate.

We first address the way in which we may exploit the strong antiferromagnetic coupling between the SAL and the LaXMnO (Coombes & Gehring 1998). This means that in a heterostructure the manganite and the SAL will be locked antiparallel. As the SAL is magnetized a coherent magnetic state will be induced in the manganite. This will be as strong as an applied magnetic field over a thin sample (we estimate the size of sample for this to be appreciable below.) In turn, this offers the possibility of CMR for LaXMnO sandwiched between two SALs. We must emphasize that this

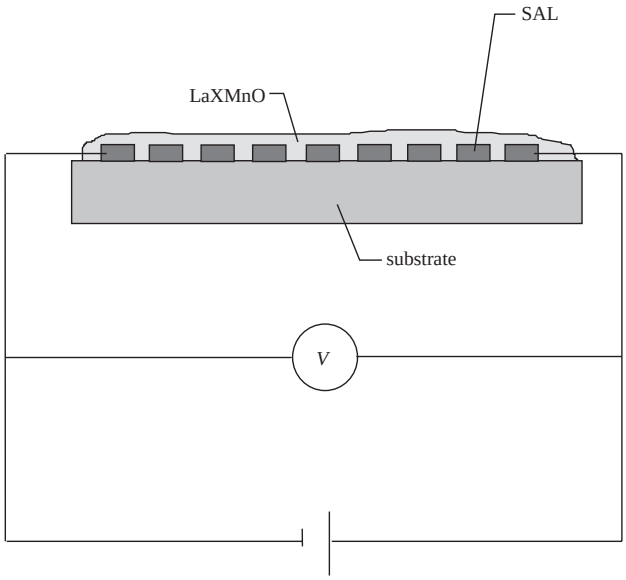

Figure 2. A schematic embodiment of a device giving a heterostructure between a soft adjacent layer (e.g. Ni) and LaXMnO. This is after Gibbs *et al.* (1998).

effect is quite different from the usual metallic magnetoresistance (e.g. in Co–Cu multilayers) in which the important scattering asymmetry arises in the magnetic metal. In our case we have the fact that the LaXMnO conduction depends on the local magnetization and this is enhanced when the Ni is in a single domain state.

The essence of our system is that we choose to arrange the structure such that a small external magnetic field acts on the SAL. The SAL magnetization will align with the field. The SAL is exchange coupled to the LaXMnO, and so the LaXMnO experiences a large exchange field from the SAL. Thus a large change in LaXMnO magnetization (and hence CMR) may come from small applied fields. This effect should be observed at high temperature just above T_C where the anisotropy field of the manganite should be zero and the manganite susceptibility large, so the paramagnetic manganite will respond readily to the exchange field of the permalloy.

The exchange interaction was calculated by using the tight binding theory to be 0.02 eV per atom. We can investigate how this energy would compare with a bulk magnetic field acting over the whole film.

We find that the product Bl may be given in terms of J_s (the interface exchange), the lattice spacing, a_0, the Bohr magneton and the g value as

$$Bl = \frac{J_s a_0}{g\mu_B} = 5.2 \times 10^{-8}\ \mathrm{T\ m}, \tag{3.1}$$

where l is the thickness of the manganite film.

For a film thickness comparable with the spin correlation length, $l = 300 \times 10^{-9}$ m, we find that the exchange interaction can give an ordering energy which is comparable with a magnetic field of $B = 0.17$ T acting over the whole film. It is important to note that the effect of the interface propagates across the width of the manganite as a result of the substantial susceptibility around the Curie point.

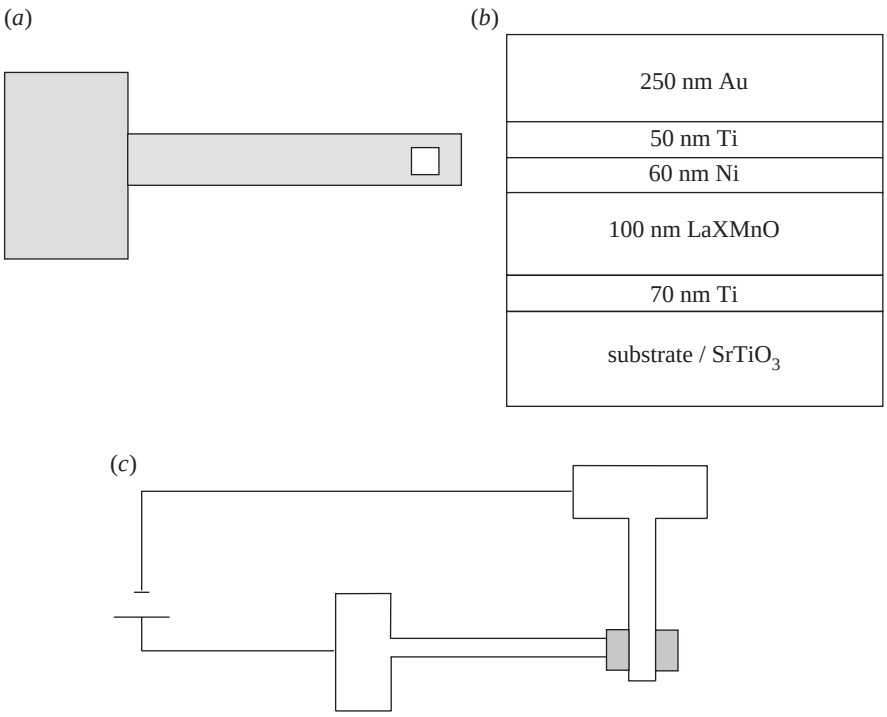

Figure 3. A schematic representation of a device using CPP geometry: (*a*) loop-shaped bottom T-bar contact; (*b*) side view; (*c*) top view of full circuit with both T-bars in place.

The practical embodiment of the heterostructure raises several issues, some of which are still to be resolved. The exchange coupling will affect both the state of magnetization of the manganite and also the interface resistance between the SAL and the manganite.

4. General features of the proposed heterostructure

This result offered above for l puts a geometrical constraint on any structure designed to probe this effect. The LaXMnO layer may only be of the order of a few hundred nanometres thick, between the SAL. Figure 2 is a schematic diagram of one possible embodiment to achieve such a device using CIP (current in plane) geometry.

The substrate is chosen to give good epitaxy ($SrTiO_3$ or $LaAlO_3$), and thus LaXMnO with a critical temperature close to ambient. The SAL material (e.g. Ni) is deposited, and then patterned, lithographically, to give mesas with a spacing no greater than the spin coherence length. This is a severe restriction, and if the spin coherence length is as short as the simple ideas above would suggest, then this may not be a practical device. The mesas are overcoated with LaXMnO to achieve the heterostructure. Current is injected and collected via suitable SAL mesas. The CIP geometry thus has constraints of spin coherence length and potential problems with the high-temperature growth for the LaXMnO degrading the SAL's magnetic properties.

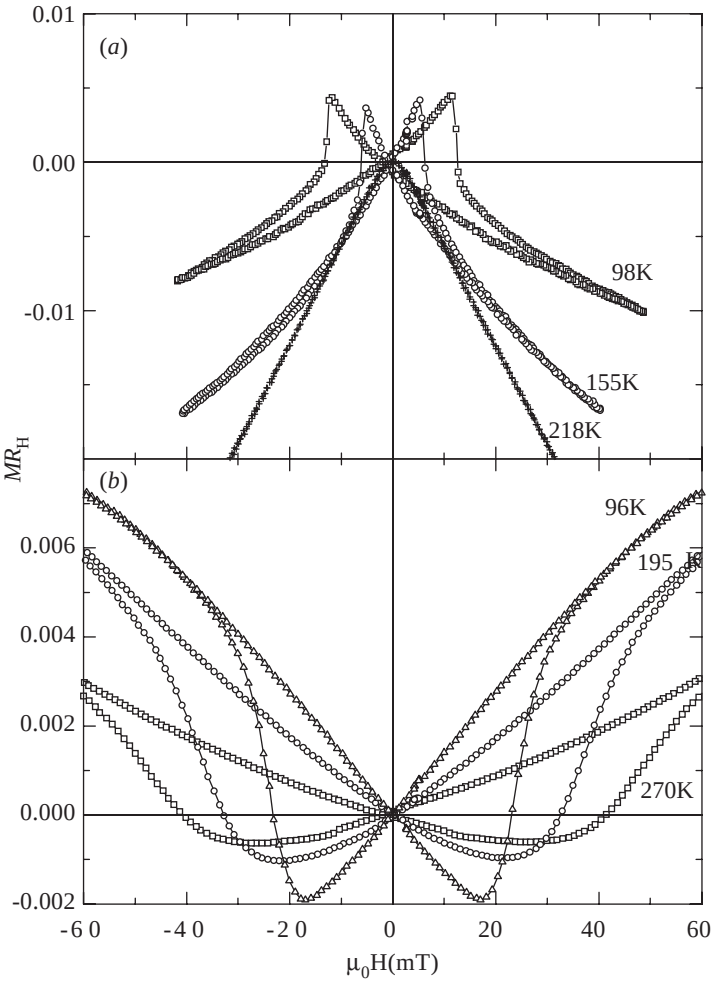

Figure 4. Magnetoresistance loops for (*a*) LaCaMnO on $LaAlO_3$ and (*b*) Ni on LaCaMNO films at a range of temperatures.

We have also considered a current perpendicular to plane (CPP) geometry, where the LaXMnO can be kept thin more easily. Care has to be taken in CPP geometry to circumvent the potential loss of epitaxy associated with the presence of the bottom SAL layer. Figure 3 is a schematic representation of our CPP structure. Ti is chosen as the basic electrode material, as both Ti and its oxide are conductors, thus alleviating the problems associated with high-temperature growth of the LaXMnO. The bottom electrode is deposited on to the substrate, and then lithographically patterned to give the loop-shaped contact (T-bar) as shown in figure 3*a*. The loop is there to ensure maximum contact of the LaXMnO with the substrate during growth, thus ensuring epitaxy and high transition temperature in the film. Ni is coated on to the LaXMnO as the SAL, and then Ti and Au are deposited on top for electrical contact. Figure 3*b* illustrates the vertical sequence of layers. The top Ti and Au are again in the form of a T-bar as shown in figure 3*c*.

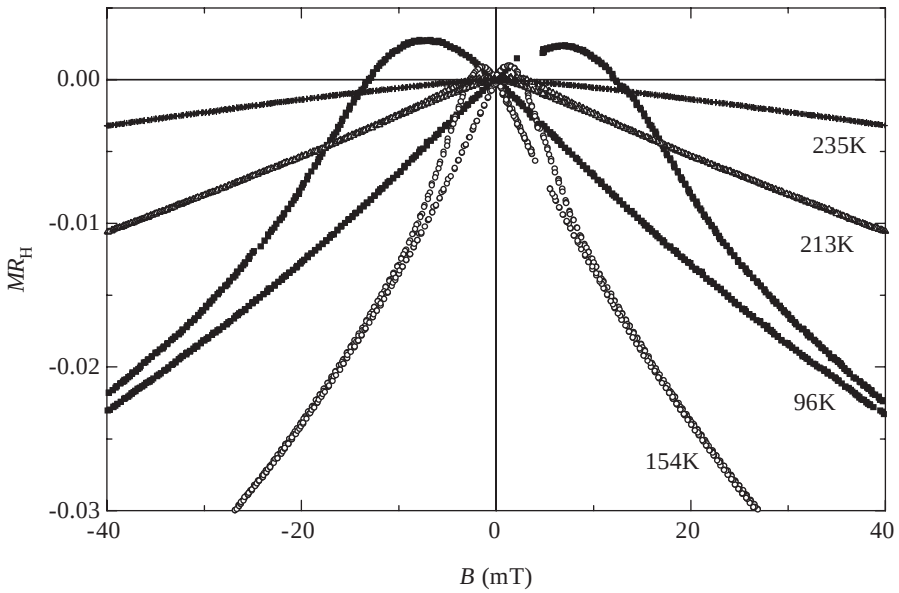

Figure 5. CPP magnetoresistance of a Ti–Ni–LaCaMnO–Ti heterostructure, as a function of magnetic field at different temperatures. The measurements are performed at a fixed current of 100 μA.

5. Practical structure

We chose to grow $La_{0.7}Ca_{0.3}MnO_3$ by pulsed laser ablation (PLD) (XeCl, 308 nm) from a stoichiometric target at an oxygen partial pressure of 100 mTorr and a substrate temperature of 720 °C. High-quality epitaxial films were produced by this route on $LaAlO_3$ and $SrTiO_3$ substrates with an as-deposited transition temperature, T_C, of 230 K, and a temperature for the resistivity maximum in zero field, T_R, of 236 K. A post-annealing treatment for 2 h at 950 °C in flowing oxygen yielded films with T_C of 280 K and T_R of 290 K. These results compare very favourably with literature values (Snyder *et al*. 1996).

To fabricate the CPP structure we first deposited a 70 nm Ti layer on $LaAlO_3$, and then etched it into the bottom T-bar. In the next step a 100 nm $La_{0.7}Ca_{0.3}MnO_3$ film was deposited by PLD using the above parameters. Then a 60 nm Ni layer was grown on top of the LaCaMnO. The LaCaMnO and Ni were patterned into small squares for the CPP measurements. Finally, another 50 nm Ti layer and a 250 nm Au layer were evaporated and the top T-bar patterned and bonded with gold wires. The contact areas, i.e. the effective overlap between top and bottom electrode, were 37×37 or 70×70 μm^2. The Ti loop was approximately 50×50 μm^2 and 4 μm in width or 98×98 μm^2 by 7 μm in width, respectively. A standard contact configuration was used for CPP studies (Pratt *et al*. 1991).

6. Spin-polarized carrier injection

From the discussion above, we might expect switching from a low to a high resistance state if the magnetization of the SAL (Ni) and LaCaMnO change their relative orientation from antiparallel to parallel (Coombes & Gehring 1998; Gibbs *et al*. 1998).

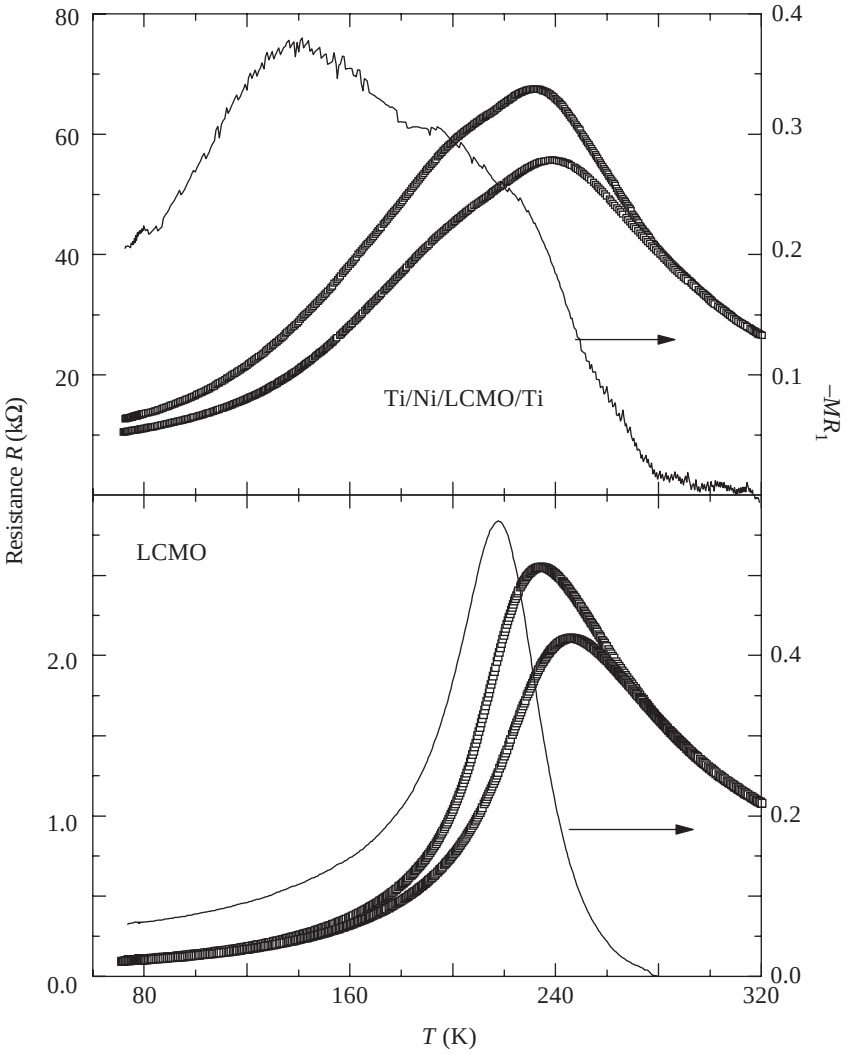

Figure 6. A comparison of the temperature-dependent transport in a Ti–Ni–LaCaMnO–Ti heterostructure and a LaCaMNO film.

We first of all established the properties of LaCaMnO and Ni layers separately. The LaCaMnO was grown on $LaAlO_3$ and the Ni on LaCaMnO. The latter is acceptable as $R_{\mathrm{LCMO}}/R_{\mathrm{Ni}} \approx 1000$. In figure 4 the longitudinal (CIP) magnetoresistance ratio (defined by equation (1.1)) of a LaCaMnO manganite and an Ni film are shown as a function of magnetic field at a range of temperatures. The curves exhibit maxima (LaCaMnO) and minima (Ni) at the respective coercive fields of the films (11 mT for LaCaMnO and 32.5 mT for Ni at 96 K). The measured coercivity for Ni is high, but comparable with other studies (Viret *et al*. 1996).

In figure 5 the magnetoresistance ratio of a heterostructure is shown as a function of magnetic field. At 96 K $M_{\mathrm{r}}(H)$ shows a maximum for $\mu_0 H = 7.5$ mT. We report elsewhere (Ziese *et al*. 1998) that the resistive properties of our current CPP devices are due to a highly resistive interface layer. This interface layer has ferromagnetic

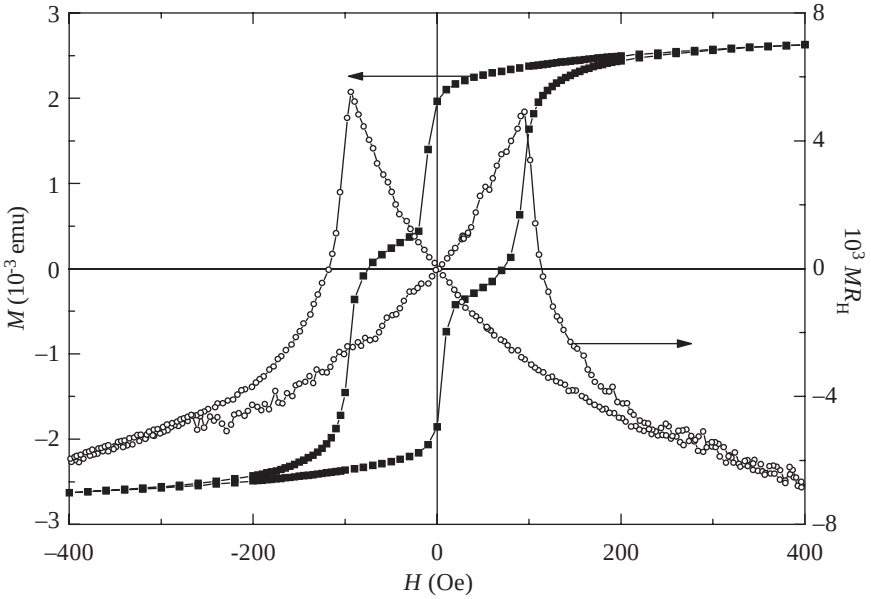

Figure 7. The magnetic and magnetotransport loops of a NiFe–LaCaMnO bilayer. These measurements taken at 100 K.

properties, thus giving a large magnetoresistance. The coercive field we see in the current CPP devices is, we believe, the coercive field of this interface layer. The LaCaMnO shows in presence through T_C only, and it is clear from figure 6 that the peak in the heterostructure magnetoresistive response is very close to the peak in the LaCaMnO response. This does indicate that epitaxy is effective using the loop-shaped T-bar bottom Ti electrode.

In figure 7 we show the hysteresis and MR loops for a NiFe–LaCaMNO bilayer structure of sufficient size for SQUID (superconducting quantum interference device) work. The switching field of the NiFe is clearly below that of the LaCaMNO, but the MR plot, measured in CIP geometry, shows no evidence of switching in the NiFe layer. Work continues to put NiFe into the full CPP heterostructure for evaluation, and to further explore the properties of the interface layer.

7. Conclusions

While the physics of a possible CPP heterostructure has been established, work remains on the understanding and control of transport in heterostructures. Issues remain in terms of the oxidation state of the SAL, and the effect of the interface itself in terms of electron scattering.

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Discussion

N. D. Mathur (*University of Cambridge, UK*). I'm impressed Dr Gibbs got epitaxy through the window. How was the window made? Was it by ion milling, and were any special precautions taken to ensure that the surface was clean afterwards?

M. R. J. Gibbs. Yes, it was ion-beam milled, and as far as I know no special precautions were taken—we used standard methods for patterning the Ti.

R. Hardiman (*Seagate Technology, UK*). In the subsequent processing of the SAL layer, were any difficulties created when Dr Gibbs had to pattern the manganite film below?

M. R. J. Gibbs. When I showed the response of the manganite film in the heterostructure, it had had all the processing done on it, and it is no different in terms of its resistance versus temperature to manganite grown on strontium titanate. So I would cite that as evidence that all the processing steps have not done anything to the manganite layer.

J. Z. Sun (*IBM T. J. Watson Research Center, NY, USA*). What are Dr Gibbs's estimates of the interface resistance between the permalloy and the manganite and between the Ni and the manganite?

M. R. J. Gibbs. I do not have a number in my head, but it is enormous. So you get huge interface resistances between Ti and LCMO, between Au and LCMO, and between Ni and LCMO.

T. Venkatesan (*University of Maryland, USA*). What would be a good, convincing reason to resort to permalloy and the oxide system when they are already producing very good spin tunnelling devices based on permalloy and other conventional magnetic systems? What is the advantage that we bring in with the oxides when we try and integrate them?

M. R. J. Gibbs. I would put forward two arguments. First, in a sense this is a bistable device: you are either turning the manganite conductivity on or off, so it is truly a digital head. There is going to be quite a sharp transition with this route of applying a soft layer next to it. Secondly, bearing in mind the requirements for high bit density, this is a structure which can very comfortably be used edge-on.

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