Magnetic and nonmagnetic tunnel barriers in \( \text{Sr}_2\text{FeMoO}_6 \)

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Abstract. Tunnelling magnetoresistance (TMR) in polycrystalline \( \text{Sr}_2\text{FeMoO}_6 \) has been a matter of intense interest for more than a decade now, where the nature of the insulating tunnel barrier turned out to be the core issue of debate. Other than the nonmagnetic grain boundaries as conventional tunnel barriers, intragrain magnetic anti-phase boundaries (APB) as well as magnetically frustrated grain surfaces have also been proposed to act as tunnel barriers and influence the TMR response of \( \text{Sr}_2\text{FeMoO}_6 \) in different ways. In this paper, it is shown that depending upon the physical state of the sample, at least three different types of tunnelling mechanism may persist in polycrystalline \( \text{Sr}_2\text{FeMoO}_6 \) and a purely conventional TMR response, seldom reported in this important magnetoresistive material, is also possible.

1. Introduction

\( \text{Sr}_2\text{FeMoO}_6 \) had been identified as an important magnetoresistive (MR) material more than a decade ago [1]. The high ferromagnetic Curie temperature (\( T_C \sim 420\text{K} \)) and the consequent room temperature MR response at lower applied field [1] had enhanced curiosity considering the technological implication. The half-metallic ferromagnetic (HMFM) nature with large spin-polarization of conduction electrons [1, 2, 3], as well as the significant contribution of polycrystalline grain boundaries in the MR response [4] established \( \text{Sr}_2\text{FeMoO}_6 \) as a representative member of TMR class of materials. However, a serious debate about the nature of the tunnel barrier evolved from the fact that the double perovskite crystal structure as well as the involved magnetic ions in \( \text{Sr}_2\text{FeMoO}_6 \) could accommodate a special kind of order-disorder fluctuation [5, 6] which could also generate insulating but magnetic tunnel barriers that can intrinsically exist irrespective of the grain nature of the samples. The core idea was that the ideally alternating Fe/Mo occupancy at the perovskite \( \text{B} \)-site could be easily disrupted in \( \text{Sr}_2\text{FeMoO}_6 \) [5] giving rise to patches of Fe-O-Fe antiferromagnetic insulating regions (APBs) which could also act as tunnel barrier between two adjacent Fe/Mo ordered HMFM domains. Therefore, two alternative mechanisms were simultaneously discussed. In one, the intergrain tunnelling was considered important with physical grain boundaries acting as tunnel barriers, [7] while in the other, the intragrain APBs have been considered to be the main component of the observed TMR [8]. To end the controversy it was needed to independently vary the contributions of these two components and probe the effect on the MR, but it turned out to be a difficult task due to the following reasons. Any attempt to increase Fe/Mo ordering (i.e. reducing the density/thickness of the APBs) by

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thermal annealing also simultaneously changed the grain morphology, thereby affecting the intergrain TMR. Moreover, the degree of spin polarization of the conduction electrons was also found to get affected by increasing disorder [2] which further complicated the situation.

Few years ago, we had tried to vary the intergrain and intragrain barriers separately and concluded in favour of the intergrain tunnelling [9] as the dominating contribution to the observed TMR. In doing so, it was assumed that the intergrain tunnelling mechanism remains unaltered between a well annealed piece of sample and a cold-pressed pellet where grains are only physically connected to each other [9]. However, our study revealed unusual magnetic responses in intergrain TMR of cold-pressed samples indicating presence of distinct magnetic states at the grain surfaces. This particular behaviour was termed as spin-valve-type MR (SVMR) although the exact SVMR mechanism was revealed only later [10]. Now it is established that the surface of each ferromagnetic grain of Sr$_2$FeMoO$_6$ possesses a frustrated spin structure which interacts with the ferromagnetic core and consequently, strong exchange bias effect is seen in the field cooled MR measurements [10, 11]. This exchange biasing is intricately connected with the existence of the frustrated surface spin structure and SVMR. In any case, it was concluded that even the intergrain tunnelling in SFMO is far from conventional due to the magnetic nature of the grain surfaces, acting as tunnel barriers [9, 10], which influences the TMR response in a unique way.

In this paper, we show that all three possible TMR responses (intragrain tunnelling across APBs, intergrain tunnelling across magnetic barriers or SVMR and conventional intergrain tunnelling across nonmagnetic barriers) could be accessed in Sr$_2$FeMoO$_6$ by controlling the physical state of the sample under study. It is also established that the intragrain tunnelling contribution cannot be ignored and in fact, most of the available reports so far presented MR data having significant share from such magnetoresistance responses.

2. Experimental

Well annealed, highly ordered sample was prepared using conventional solid state route [1, 5] at 1250°C. One such pellet was thoroughly crushed in mortar and pestle and then a cold-pressed (CP) pellet was formed at room temperature. Different pieces from a CP pellet have been annealed at 300°C, 600°C, and 900°C. These low temperature annealing could not affect the degree of ordering as the samples were formed at much higher temperature (1250°C), while the grain connectivity was affected because the grains were loosely connected in CP samples. In another attempt, melt-grown pieces were grown in a vacuum arc furnace following the method described in Ref. 5. The as-grown sample possesses large degree of disorder, as reported earlier [5, 12]. Following this, pieces of such molten ingots were annealed at 900°C, 1100°C, 1250°C, 1350°C, and 1500°C. Here, the annealing could hardly affect the grain connectivity as large crystalline grains were already well connected in the molten samples, but could influence the Fe/Mo ion-ordering through high temperature ionic diffusion. The extent of ordering in all these samples was probed by x-ray diffraction studies, carried out in Bruker AXS: D8 Advance x-ray diffractometer with Cu $K_a$ radiation. Magnetoresistance as a function of $H$ ($MR(H)$) was measured on all these samples using a Cryogenics PPMS system and also a homemade resistivity measurement setup, equipped with a low-field electromagnet.

3. Results and discussion

The XRD studies (not shown here) confirmed that the degree of ordering did not improve by annealing the CP sample at 300°C, 600°C, and 900°C. Then, the SVMR behaviour was probed by measuring the exchange bias signal in $MR(H)$ measurements. In this measurement, the samples were at first cooled under an applied magnetic field of 2000 Oe down to 10 K. Then the field was switched off and the $MR(H)$ measurement was carried out at 5 K with the maximum measurement field being at least few times higher than the highest irreversibility field of the corresponding $M(H)$ data in order to avoid any minor loop effect [10]. The results of such measurements on the CP, and 300°C, 600°C, and 900°C annealed samples are shown in figure 1(a). Evidently, the cold-pressed sample exhibited large exchange biasing, reminiscent of the SVMR effect [10]. Interestingly, the exchange bias tends to
decrease gradually with increasing annealing temperature and finally disappears in case of the 900ºC annealed sample. This clearly indicates that annealing triggers chemical bonding between the neighbouring grains which adversely affects the frustrated surface spin structure and as a result SVMR disappears. This is more clearly shown in figure 1(b), where the exchange bias field ($H_E$) has been plotted as a function of annealing temperature. It is observed that an exchange bias field of 200 Oe in case of the CP sample goes to zero in the sample annealed at 900ºC. One important conclusion that could be drawn from this observation is that SVMR operates only in polycrystalline samples with loosely connected grains while it becomes insignificant in case of well annealed samples. Therefore, as most of the literature discussed only well annealed samples, one can safely conclude that SVMR response could at the most be negligible in those data and therefore, would not qualify to participate in the running controversy about the nature of tunnel barrier in the TMR response of the highly annealed samples.
The XRD data from the pieces of molten ingots, annealed at 900°C, 1100°C, 1250°C, 1350°C, and 1500°C are shown in figure 2. The regular increase in the intensity of the superlattice peak establishes that the degree of ordering could indeed be improved by higher temperature annealing.

In figure 3(a), the $MR(H)$ data from the molten ingots, annealed at 900°C, 1100°C, 1250°C, 1350°C, and 1500°C are shown. Evidently, the nature of the $MR(H)$ has undergone a large variation from 900°C annealed piece to the 1500°C. It is to be noted that all these pieces contain large physical grains and small density of physical grain boundaries while the degree of Fe/Mo disorder is expected to be different from sample to sample. The 900°C annealed sample shows no sharp low-field $MR$ (LFMR) and varies almost linearly to reach a value of 11% at 7 Tesla. This behaviour is very similar to the

![Figure 3. (Colour Online) The $MR(H)$ behaviours at 5K for the molten ingots, annealed at 900°C (full circle), 1100°C (full triangle), 1250°C (open circle), 1350°C (open square), and 1500°C (asterisk) are shown in the upper part. The lower panels (a), (b), (c) are expanded schematic representations of $B$-site ordering about a grain boundary (dark lines) for different annealing temperatures of the molten ingots. Red and blue spheres represent ordered Fe and Mo atoms while gray and green spheres represent the same ordered atoms shifted i.e. red, blue and gray, green portions represent ordered Fe, Mo regions connected through antiphase relation.](image)

behaviour of the as-grown ingot [5], which indicates that an annealing at 900°C hardly affects the degree of ordering. Interestingly, the nature of $MR(H)$ curve starts to change substantially for samples annealed at or above 1100°C, where a TMR-like sharper low-field response starts to become visible. As the density or thickness of the physical grain boundaries do not change within this range and also there is no effect of SVMR, one can conclude that this observed TMR-like response must clearly be a manifestation of changing density or thickness of the APBs. Considering the fact that the $MR$ goes above 17% for the sample annealed at 1350°C at 7 Tesla, it can be argued that the intragrain TMR across APB contributes significantly to the observed TMR of polycrystalline Sr$_2$FeMoO$_6$.

We had recently shown that the description of disorder in Sr$_2$FeMoO$_6$ is in reality very different in contrast to previous understanding [13]. The proposed scenario is schematically shown in panel (a) at the lower part of figure 3. It was observed that even in the so-called highly disordered sample, the local Fe/Mo ordering remains quite high [13] and the traditional disordering picture needs to be replaced by a description of nano-sized highly ordered domains connected via antiphase relationship (the sharp boundaries between the red-blue and gray-green regions). Contrary to previous prediction [2], the degree of spin-polarization is expected to remain significantly high in these so-called highly disordered samples. However, for extremely small-sized domains it becomes rather difficult to magnetize them along the direction of the magnetic field and therefore, the $MR(H)$ remains linear as in the case with 900°C annealed sample. However, with increasing annealing temperature, the domains increase in size (panel (b)) and a nearly bulk-like magnetic behaviour is achieved. As a result, TMR-
like response across APBs starts to dominate, as seen in $MR(H)$ curves of figure 3. However, the most astonishing result is observed in case of the sample annealed at 1500°C. Suddenly, both the nature of the $MR(H)$ curve and the magnitude of $MR$ changes. It is worth mentioning here that the same reversal was also observed earlier (see figure 1(b) of Ref. 9) although was not analyzed in detail. The most distinct features of this $MR(H)$ curve is the presence of large low-field $MR$ response as is normally observed in other conventional TMR materials like manganites [14] as well as a strong decrease in $MR$ value (10% at 7 Tesla). It appears that the tunnelling mechanism transforms into the conventional one where only the nonmagnetic, insulating grain boundaries act as tunnel barriers and the TMR response is completely dominated by the low-field alignment of the magnetic grains, resulting in large LFMR signals. It can be argued that annealing at 1500°C practically removes all the APBs (see panel (c)) and as a result only the conventional TMR retains. The low density of the physical grain boundaries in the ingots naturally reduces the TMR value. Overall, it appears that the intragrain TMR across APBs contribute heavily in samples annealed between 1000°C and 1500°C and the nature of the $MR(H)$ curves exhibit distinct differences (low LFMR and gradual changes) as compared with conventional TMR. It is important to note here that most of the results available in the literature fall into this category including Ref. 1 and it is expected that all the reported data had a mixed TMR response and the conventional TMR response in Sr$_2$FeMoO$_6$ is rarely observed.

4. Conclusion

In summary, we have shown that three different TMR mechanisms can operate in polycrystalline SFMO and the relative contributions could be easily controlled by carefully manipulating the grain connectivity and disorder density. SVMR type $MR$ dominates in samples with poor or no grain connectivity while it disappears after annealing above 900°C. TMR across APBs does have significant contribution till a perceptible amount of APBs exist. In this case, the $MR(H)$ curves do not contain large LFMR signal which is a characteristic difference with the conventional TMR signal. Lastly, annealing at highly elevated temperatures (~1500°C) get rid of all the APBs and only the conventional TMR across nonmagnetic physical grain boundaries remain, which is characterized by a sharp LFMR response.

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