Inter-grain tunnelling in the half-metallic double-perovskites Sr₂BB'O₆ (BB'= FeMo, FeRe, CrMo, CrW, CrRe)

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Abstract. The zero-field conductivities (σ) of polycrystalline title materials, are governed by inter-grain transport. In the majority of cases their σ(T) can be described by the "fluctuation induced tunnelling" model. Analysis of the results in terms of this model reveals two remarkable features: 1. For all Sr₂FeMoO₆ samples of various microstructures, the tunnelling constant (barrier width × inverse decay-length of the wave-function) is ~ 2, indicating the existence of an intrinsic insulating boundary layer with a well-defined electronic (and magnetic) structure. 2. The tunnelling constant for all cold-pressed samples decreases linearly with increasing magnetic-moment/formula-unit.

1 Introduction

Half-metallic ordered double-perovskites with fully polarized conduction bands and Curie temperatures (Tc) above room temperature (RT) are of interest for devices which depend on spin polarized transport. Therefore their magnetic, electronic and in particular their magneto-resistive properties [1] have been investigated intensively over the past two decades. The grain boundaries in these materials act in most cases as tunnel barriers. The early theories of inter-grain magneto-resistance due to tunnelling through a non-magnetic barrier separating two ferromagnetic grains (including vacuum) [2-4] could not explain inter-grain magneto-resistance in half-metals. Polycrystalline and cold-pressed Sr₂FeMoO₆ (SFMO) samples with identical metallic thermopower (bulk properties) exhibited very different zero-field and magneto-conductance [5]; it was proposed that this difference is due to different magnetic properties of the grain-boundaries. The magneto-resistive behaviour of (Ba Sr)₂FeMoO₆ [6] was explained in terms of tunnelling between two correlated spin glass-like surfaces separated by a thin insulating layer. The magnetization and magneto-resistance (MR) data for a series of SFMO samples [7] were interpreted in terms of a model in which the grain-boundary regions act as spin valves; this MR was termed SVMR. It was shown [8] that SVMR is a generic feature of the metallic, ferromagnetic double-perovskite family as a whole. Careful ac susceptibility measurements on a highly ordered polycrystalline sample of SFMO [9] were able to separate the barrier layer signal from the bulk. The presence of an intrinsic insulating boundary layer, about 2 unit cells thick, around grains of (La Sr)MnO₃ with magnetic properties different from those of the bulk [10], is held responsible for the depressed magneto-transport properties in manganite based magnetic junctions.

Unlike the difficulty in separating the magnetic properties of the layers from those of the bulk [9], it is relatively easy to study the electronic properties of the grain skin layers when the electronic transport is dominated by inter-grain tunnelling as is the case in most of the polycrystalline samples of the title materials. In this report we focus on the zero-field conductivity of various samples of the five title compounds using results accumulated in this lab. Some of the unpublished results will be presented for the first time here. This comparative study revealed some important features of the grain-boundaries of these half-metals.

2.1 Inter-grain tunnelling in Sr₂BB'O₆

Table I shows the five title double-perovskites (with abbreviations), their ionic configuration, nominal (ideal) saturation magnetization (M₀) and Tc. While the bulk of these materials is metallic, as confirmed by their metallic-like thermopower [12], the zero-field conductivities (σ(T)) of polycrystalline samples are non-metallic (the conductivity increases with increasing T). Metallic-like resistivity was found in a single crystal of SFMO [13]. The inter-grain tunnelling conductivity depends strongly on preparation conditions and often exhibits unusual T-dependence. The most remarkable behaviours are the linear-in-T conductivities from liquid He temperatures up to RT, for all our sintered and granular samples of SFMO, irrespective of preparation conditions, for some samples of SFRO and of SCMO, and the linear-in-T²...
conductivity over the same range of T, for some samples of SCMO [14].

Table 1. The five Sr2BB’O6

| Sr2BB’O6  | Ionic configuration | Mf | 1000 (K) |
|-----------|---------------------|----|---------|
| Sr2FeMoO6 (SFMO) | Fe⁺⁺⁺(3d8)Mo⁺⁺⁺(4d1) | 4  | 420     |
| Sr2FeReO6 (SFRO) | Fe⁺⁺⁺(3d8)Re⁺⁺⁺(5d1) | 3  | 400     |
| Sr2CrMoO6 (SCMO) | Cr⁺⁺⁺(3d8)Mo⁺⁺⁺(4d1) | 2  | 450     |
| Sr2CrWO6 (SCWO) [11] | Cr⁺⁺⁺(3d8)W⁺⁺⁺(5d1) | 2  | 390     |
| Sr2CrReO6 (SCRO) | Cr⁺⁺⁺(3d8)Re⁺⁺⁺(4d1) | 1  | 635     |

The temperature dependence of the conductivity for all our samples, except for porous SCRO, can be derived from the "fluctuation induced tunnelling" (FIT) model [15]. This model applies to metallic grains embedded in an insulating medium. Tunnelling occurs across small gaps (width w and area A) between large metallic grains; the small gaps are subject to large thermal fluctuations of the voltage. \( \sigma(T) \) predicted by this model is:

\[
\sigma = \sigma_0 e^{-\frac{T_1}{T_1+T}} = \sigma(0) e^{-\frac{T_1}{T_1+T}}
\]

where \( k_B T_1 = (2\pi k_B \alpha A w/w_c)^2 \) is the electrostatic energy within a parabolic potential barrier of width w and height \( V_c \) of a junction of area \( A \), \( T_1/T_c = \pi k_B \alpha A w/w_c \) is the tunnelling constant where \( \alpha = \sqrt{\frac{2}{3}} \). \( \sigma_0 \) is a pre-exponent that may be regarded as independent of temperature and \( \sigma(0) = \sigma_0 \exp(-T/T_c) \). The FIT equation for \( \sigma(T) \) is an extension of the formula derived for a single junction to a network of fluctuating tunnelling junctions [15]. For \( T < T_c \), Eq. (1) represents elastic tunnelling and for \( T > T_c \) - activated conductivity with activation energy \( k_B T_1 \). The effect of the thermal fluctuations is to reduce the barrier’s height and width; for \( T = T_c \) the effective tunnelling constant is half its value at \( T = 0 \). This equation includes the unusual and interesting cases mentioned above for the specific ranges of the parameter \( T_1/T_c \) and of \( T/T_c \). In Ref. [14] we showed that for \( T_1/T_c < 1 \) a linear function of \( T \) fits \( \sigma(T) \) over a \( T/T_c \) range that increases with \( T/T_c \). The correlation parameter of the linear fit to Eq. (1) for \( T_1/T_c \leq 3 \) and \( T/T_c \leq 1.1 \) is \( R^2 = 0.9999 \). In this range, \( \sigma(T) \) varies up to a factor of 5, in good agreement with our findings (see figure 4 in Ref. [14]). We showed also that \( \sigma(T) \) obeys the FIT model with reasonable parameters (see below).

The FIT model does not address magnetic interactions. Since it was applied successfully to at least three groups of magnetic materials (our title materials, CrO2 and its composites [19, 20] and Co-based nanocomposites [21]), it may be assumed that the influence of the magnetic interactions affect the nature of the tunnelling barrier and the pre-exponent. As \( M_f \) of our samples varies between 1 and 4, we attempted to detect correlations between the tunnelling parameters of the exponent of Eq. (1) and \( M_f \).

2.2 Experimental results and discussion

Table 2 contains the fitting parameters of Eq. (1) to the experimental \( \sigma(T) \) : \( \sigma(0) \), \( T_1 \), \( T_c \) and \( T_1/T_c \), for our samples of Sr2BB’O6. The labels of the five groups of samples and data sources (references to our previous publications and figures 1 and 2 shown here), are followed by the fitting parameters. Only two parameters in the exponent are independent, but for convenience all three are shown (\( T_1 \), \( T_c \) and \( T_1/T_c \)). We also show the fitted parameters for a cold-pressed Sr1.4La0.6FeMoO6 (LSFMO). Additional plots of \( \sigma(T) \) for SFMO are shown in Ref. [18]; all are straight lines up to RT. The slopes of the plots for the cold-pressed samples are steeper than those for the sintered samples. The conductivities of the samples at \( T = 0 \) \( \sigma(0) \), spread over many orders of magnitude, from \( 10^{-6} \) to \( 10^2 \) (\( \text{Ωcm})^{-1} \). The highest \( \sigma(0) \), \( \sigma(0) = 74.5 \text{ (Ωcm)}^{-1} \), for sample SFMO(N1)) is about 50 times lower than the metallic conductivity of an SFMO single crystal at \( T = 0 \) [13].

The upper curve in figure 1(a) shows \( \sigma(T) \) of a sintered SFRO sample that underwent a short heat treatment at 500°C in Ar5%H2. The maximum indicates mixed grain-boundary and metallic conductivity. A similar behaviour is seen in Figure 2 of Ref. [22] for an SFRO sample sintered in an Ar atmosphere. Prolonged heat treatment of
Table 2. Fitting parameters for Eq. (1), for Sr$_2$BB'O$_6$ polycrystalline samples

| Sample, figure, [Ref.] | $\sigma(0)$ (Ω cm)$^{-1}$ | $T_1$ (K) | $T_0$ (K) | $T_1/T_0$ |
|------------------------|--------------------------|----------|----------|-----------|
| SFMO(N1) 2, [18]       | 74.5                     | 5171     | 2478     | 2.09      |
| SFMO(r) 4, [14]        | 33.8                     | 6989     | 2551     | 2.74      |
| SFMO(c.p.) 2, [14]     | 0.72                     | 1586     | 582      | 2.73      |
| SFRO(Ox) 1(a), here    | 2.50                     | 396      | 494      | 0.80      |
| SFRO(S1) 1(b), here    | 3.88                     | 1117     | 703      | 1.59      |
| SFRO(S2) 1(b), here    | 13.0                     | 276      | 397      | 0.70      |
| SFRO(c.p.) 1(b), here  | 0.19                     | 8111     | 1329     | 6.10      |
| SCMO(A) 2(a), [14]     | 1.02                     | 712      | 263      | 2.71      |
| SCMO(C) 2(a), [14]     | 2.48                     | 455      | 117      | 3.39      |
| SCMO(E) 2(a), [14]     | 6.10                     | 390      | 130      | 3.00      |
| SCMOA+Ox) 2(a), [14]   | 4.6×10$^{-4}$            | 1104     | 207      | 5.33      |
| SCMO(D1) 2(b), [14]    | 0.31                     | 1405     | 228      | 6.16      |
| SCMO(B1) 3(b), [14]    | 6.3×10$^{-4}$            | 1430     | 180      | 7.94      |
| SCMO(B2) 3(b), [14]    | 5.6×10$^{-4}$            | 1177     | 152      | 7.74      |
| SCWO 6(a) [11]         | 0.045                    | 260      | 120      | 2.20      |
| SCWO 6(a) [11]         | 0.030                    | 461      | 213      | 2.16      |
| SCWO(c.p.) 2, here     | 2×10$^{-5}$              | 1850     | 200      | 9.25      |
| SCRO(c.p.) 2, here     | 1.2×10$^{-5}$            | 4071     | 383      | 10.63     |
| LSFMO(c.p.) 4, [14]    | 0.47                     | 941      | 298      | 3.16      |

r-reduced, c.p.-cold-pressed, Ox – oxidized

Figure 1. Conductivity versus temperature of (a) a sintered sample of Sr$_2$FeReO$_6$ heat treated at 500°C in a reducing atmosphere (upper curve) and later re-oxygenated at 400°C (lower curve), and (b) two additional sintered samples and one cold pressed sample. Solid lines in (a) and (b) represent Eq. (1) fitted to experimental data.

Figure 2 presents plots of $\sigma(T)$ for c.p. samples of SCWO and SCRO that were not included in the previous reports [11, 16]. Although the conductivities of porous SCRO samples are of Berthelot type, figure 2 shows that Eq. (1) fits $\sigma(T)$ of the c.p. sample.

The three parameters $T_1$, $T_0$, and $T_1/T_0$ are plotted versus $M_i$ in figures 3(a)-(c). $M_i$ for LSMO is 3.5. While no correlations are seen in figures 3(a) and (b), figure 3(c) exhibits two remarkable features:

1. The data of $T_1/T_0$ (the tunnelling constant $\pi \chi w/2$) for SFMO fall between 2 and 3, irrespective of microstructure of the samples. Within the FIT model this corresponds to the remarkable linearity of $\sigma(T)$. The independence from microstructure hints at the presence of an intrinsic insulating boundary layer through which tunnelling occurs, with well-defined electronic (and magnetic) structure. Note that the tunnelling constant depends only on the width $w$ and the height $V_o$ of the barrier. For a thickness $w$ of the order of the c-axis lattice constant of SFMO (=7.92 Å) and the range of $T_1/T_0$ given in Table II the values of $V_o$ range between 0.25 to 0.5 eV, far higher than $k_BT$ up to RT. This inequality is still valid for $w=2c$ but not for a much larger factor. As mentioned in the introduction, the thickness of the insulating boundary layer found in LSMO is about two unit cells, close to our estimate.

2. The data of $T_1/T_0$ for cold pressed samples (i.e. for bare boundaries) lie close to a straight line that extrapolates to zero near $M_i=5$ which corresponds to vanishing minority spins (see Table I). The possibility that such a simple analytical function fits the dependence of $\pi \chi w/2$ on $M_i$ for this set of half-metallic c.p. samples requires further experimental and theoretical support. Since the variation in the lattice parameters in this family of compounds is negligible, the steep increase in the
value of $T_1/T_o$ with decreasing $M_i$ may be due to the increase of the thickness of the insulating layer, leaving $V_o$ comparable with that of SFMO.

Fig. 3. Fitting parameters $T_1$, $T_o$ and the tunnelling constant $T_1/T_o$ as function of $M_i$. For $M_i=2$ the symbol × represents samples of SCMO and + the samples of SCWO. Encircled symbols represent data for cold pressed samples. Note that for all SFMO samples, $T_1/T_o$ falls between 2 and 2.75 (within the range of linear $\sigma(T)$). The values of $T_1/T_o$ for the cold pressed samples increase almost linearly with $M_i$.

Eq. (1) shows that the higher $T_o$ (relative to RT), the closer is inter-grain tunnelling to elastic tunnelling. Table II and figure 3(b) show that, for only 3 samples out of 19, $T_o > 1000$ K, namely for two polycrystalline samples of SFMO (in figure 3(b) the two symbols coincide) and for one c.p. sample of SFRO. Note that for all SFMO samples, $T_1/T_o$ falls between 2 and 2.75 (within the range of linear $\sigma(T)$). The values of $T_1/T_o$ for the cold pressed samples increase almost linearly with $M_i$.

The wide spread of the FIT parameters in Table II implies a broad range of magneto-conductance behaviors. Ref. [5] shows that for sintered SFMO samples the magneto-conductance is much higher than that for a c.p. sample at all temperatures. This requires a more systematic investigation.

References

1. D. Serrate, J. M. De Teresa and M R Ibarra, J. Phys. Condens. Matter 19, 023201 (2007) and references therein
2. M. Julliere, Phys. Lett. 54A, 225 (1975)
3. J. C. Slonczewski, Phys. Rev. B 39, 6995 (1989)
4. J. Inoue and S. Mackawa, Phys. Rev. B 53, R11927 (1996)
5. B. Fisher, K. B. Chashka, L. Patlagan and G. M. Reisner, J. Magn. Magn. Mater. 272-276, 1790 (2004)
6. D. Serrate, J. M. De Teresa, P. A. Algarabel, M. R. Ibarra, and J. Galibert, Phys. Rev. B 71, 104409 (2005)
7. D. D. Sarma, S. Ray, K. Tanaka, M. Kobayashi, A. Fujimori, P. Sanyal, H. R. Krishnamurthy, and C. Dasgupta, Phys. Rev. Lett. 98, 157205 (2007)
8. S. Jana, S. Middey and S. Ray, J. Phys. Condens. Matter 22, 346004 (2010)
9. S. Ray, S. Middey, S. Jana, A. Banerjee, P. Sanyal, R. Rawat, L. Gregoratti and D. D. Sarma, EPL 94, 47007 (2011)
10. S. Valencia, L. Pena, Z. Konstantinovic, Ll. Balcells, R. Galceran, D. Schmitz, F. Sandiumenge, M. Casanove and B. Martinez, J. Phys.:Condens. Matter 26, 166001 (2014)
11. Sr$_2$CrWO$_6$ has been confused in the past with Sr$_3$Cr$_2$WO$_9$, which has a much higher $T_c$. Preparation of these two distinct compounds as single phases was reported in: B. Fisher, K. B. Chashka, L. Patlagan, and G. M. Reisner,Phys. Rev. B 71, 104428 (2005)
12. B. Fisher, J. Genossar, K. B. Chashka, L. Patlagan and G. M. Reisner, Curr. Appl. Phys. 7, 151 (2007)
13. Y. Tomioka, T. Okuda, Y. Okimoto, R. Kumai, K.-I. Kobayashi and Y. Tokura, Phys. Rev. B 61, 422 (2000)
14. B. Fisher, J. Genossar, K. B. Chashka, L. Patlagan, and G. M. Reisner, Solid State Commun. 137, 641 (2006) and references therein
15. Ping Sheng, Phys. Rev. B 21, 2180 (1980) and references therein
16. B. Fisher, K. B. Chashka, L. Patlagan, and G. M. Reisner, Phys. Rev. B 70, 205109 (2004)
17. R. H. Tredgold, Proc. Phys. Soc. London 80, 807 (1962)
18. B. Fisher, K. B. Chashka, L. Patlagan, and G. M. Reisner, Phys. Rev. B 68, 134420 (2003)
19. A. Bajpai and A. K. Nigam, Phys. Rev. B 75, 064403 (2007)
20. Fan Yin-Bo, Zhang Cai-Ping, Du Xiao-Bo, Wen Ge-Hui, Ma Hong-An and Jia Xiao-Peng, Chin. Phys. Lett. 30, 037502 (2013)
21. T. Wen and K. M. Krishnan, J. Phys. D: Appl. Phys. 44, 393001 (2011)
22. K.-I. Kobayashi, T. Kimura, Y. Tomioka, H. Sawada, K. Terakura and Y. Tokura, Phys. Rev. B 59, 11159 (1999).