Intergrain tunneling in granular Sr_2FeMoO_6 studied by pulsed high currents

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The zero-field intergrain tunneling conductivity σ of sintered and granular Sr_2FeMoO_6 increases linearly with temperature over the range ~20–300 K, at least. The residual conductivity of the investigated samples ranges over more than four orders of magnitude and the total change of σ up to room temperature ranges from ~20% in the sintered samples to a factor of 3 in granular samples. $\sigma(T)$ is hysteretic upon cycling through the Curie temperature T_c and becomes slightly superlinear above T_c. In order to identify the parameter responsible for the unusual linear T dependence, the nonlinear (electric-field dependent) conductivity of granular samples was investigated at various temperatures up to 300 K using pulsed high currents. The results indicate that the effective height and width of the potential barrier in the exponent of the current density are temperature independent, while the preexponent exhibits a linear T dependence. The significance of this result is discussed in view of the crucial role played by the preexponent in intergrain magnetoresistance.

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I. INTRODUCTION

The double perovskite Sr_2FeMoO_6 (SFMO), a half-metallic ferrimagnet,[1,2] has attracted attention due to the large low-field magnetoresistance (MR) of polycrystalline samples at room temperature (RT).[1,3] This is due to its high Curie temperature ($T_c \approx 410$ K) as well as to the nature of its grain boundaries (GB). The nonmetallic, weakly temperature-dependent resistivity ρ of single-phase, ordered polycrystalline SFMO may exceed the bulk, single-crystal resistivity[4,5] ($<10^{-3}\ \Omega\,\mathrm{cm}$) by several orders of magnitude.[1] In such samples the resistivity is dominated by intergrain tunneling.

In the course of transport and magnetotransport measurements carried out on sintered and granular SFMO,[6] we were intrigued by the unusual temperature dependence exhibited by our samples' zero-field conductivity. The RT resistivities of the granular samples (cold-pressed powder compacts) were from two to four orders of magnitude higher than that of the sintered, parent material. *For all investigated samples the zero-field conductivity σ varied linearly with temperature between* ~20 K *and RT*. In this range the total change of the resistivity ρ of our sintered sample was only ~20% and therefore linear functions could be fitted to both $\rho(T)$ and $\sigma(T)$. For the granular samples, $\sigma(\mathrm{RT})/\sigma(0)>2$ and only $\sigma(T)$ is linear.

This remarkably simple temperature dependence of σ is very different from that observed in other high-MR systems such as CrO_2 powder compacts[7,8] or manganites,[9] where intergrain conduction is governed by a combination of elastic and inelastic tunneling via impurity states. No such combination could reproduce the experimental results obtained for the granular samples.

Many systems can be modeled as consisting of large metallic regions separated by thin insulating layers, having finite (metallic) conductivity at $T \rightarrow 0$ and positive (nonmetallic) $d\sigma/dT$ for $T>0$.[10,11] In such systems electronic transport is governed by tunneling across the insulating layers. The temperature dependence of σ may be due to fluctuation-induced variations of the heights and widths of the potential barriers that appear in the exponent of the tunneling probability.[10] This model, known as fluctuation-induced tunneling (FIT), extends from elastic tunneling (that is independent on temperature) to activated hopping;[12] for a range of parameters, $\sigma(T)$ may increase linearly with T over wide ranges of temperature.[13] This model could provide a very simple and intuitive explanation to our findings. If applicable to our results, the linear temperature dependence of σ would be governed mainly by the T dependence of the *exponent* of the tunneling probability.

In the case of spin-polarized tunneling the *preexponent* of the tunneling probability depends upon the local magnetizations and their relative orientation on the interfaces between adjacent grains along the conduction path. Thus, according to present understanding MR is governed by the preexponent.[14,15] Therefore, knowing and understanding its temperature dependence is crucial for understanding MR in sintered and granular SFMO.

In order to evaluate the relative roles of the exponent and the preexponent of the tunneling probability in determining $\sigma(T)$, our measurements were extended from the Ohmic to the nonlinear (electric-field-dependent) conductivity regime. The theoretical treatment of this regime is included in the FIT model and has successfully been applied to the analyses of nonlinear J-E characteristics (J is current density and E is electric field) of many heterogeneous systems.[10,16–18] Here, the I-V characteristics were obtained using *pulsed* currents, the only technique that prevents Joule heating over a wide range of currents and verifies its absence. Electric fields up to ~300 V/cm could be applied to our most resistive sample. The J-E plots were analyzed using various expressions for field-dependent tunneling but that predicted by the FIT model gave the best results. The analysis showed that the effect of the thermal fields on tunneling is negligible and that the temperature dependence of tunneling is governed by the preexponential term.

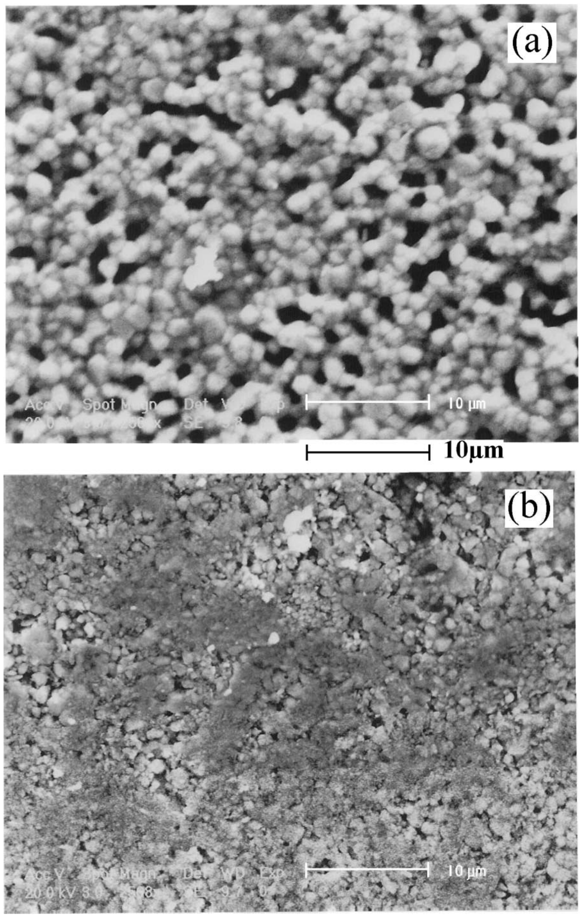

FIG. 1. Electron micrographs of a sintered (a) and a granular sample (b).

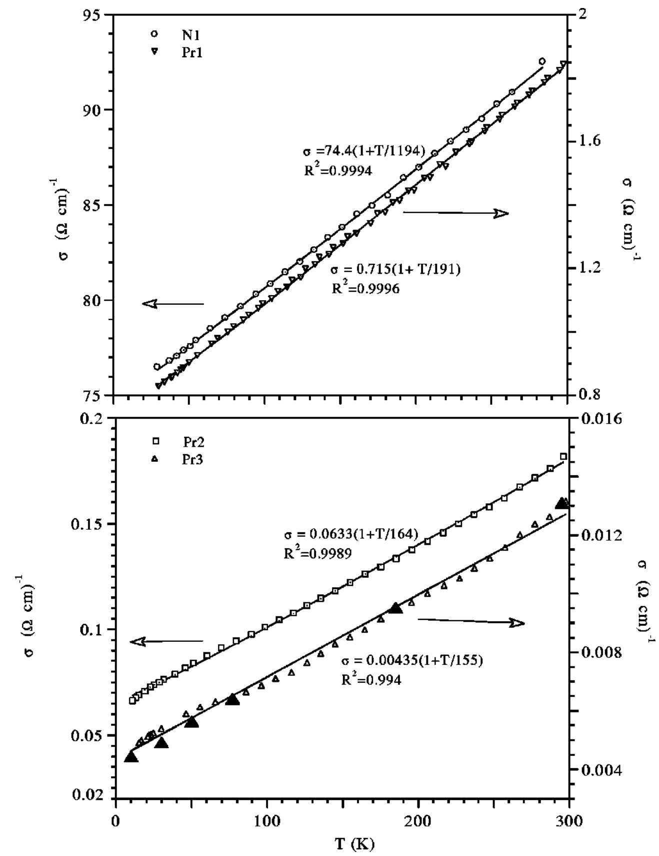

FIG. 2. σ vs T for a sintered sample N1 and granular samples Pr1–Pr3. The bold symbols represent the temperatures for which detailed *I-V* measurements were carried out on sample Pr3.

II. EXPERIMENT

Polycrystalline Sr_2FeMoO_6 has been prepared by the standard solid-state reaction as reported in Ref. 1. The x-ray-diffraction powder pattern of the compound showed no foreign phases. The granular samples were obtained by crushing and pulverizing a sintered pellet followed by pressing the powder into bars at RT. The electron micrographs of sintered and granular samples are shown in Fig. 1. The average diameter of the sintered sample's grains is ~ 2 μm; the range of granules' diameters of the other sample is wide with the largest diameters ~ 1 μm. The sintered material is rigid while the granular samples are crumbly.

The resistivity of bar-shaped sintered or granular samples was measured by the standard four-probe method in a closed cycle refrigerator or on a cold finger of a He cryostat. From RT to 450 K the resistivity measurements were carried out in separate systems, operated manually. To enable safe transfer of the granular samples for resistivity measurements, from the low-T to the high-T sample holders, their four contacts were made of gold wires embedded during compaction. Special care was taken also of the quality of the current contacts and the voltage probes of the samples on which the *I-V* measurements were carried out. At high currents, the measurements were carried out using single current pulses of durations in the millisecond range, from a Keithley 237 high voltage source. The pulsed voltage drops between pairs of probes were measured using a Tektronix 2221A digital storage oscilloscope. Beyond a finite rise time (in the microsecond range), the measured voltages showed no time dependence during the applied pulses, thus ruling out Joule heating.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The weakly temperature-dependent resistivity plots of our sintered samples were similar to those reported previously.[1] Figure 2 shows σ vs T for a sintered sample N1 and for three granular SFMO samples Pr1–Pr3. The conductivity increases linearly with T with high accuracy as shown by the correlation parameters R^2 and is expressed as $\sigma(T)=\sigma_o(1+T/T_g)$. Among the data in Fig. 2, σ_o and T_g vary by more than four orders and less than one order of magnitude, respectively. However, while $\sigma_o(\mathrm{N1})/\sigma_o(\mathrm{Pr1})\approx 100$ is accompanied by $T_g(\mathrm{N1})/T_g(\mathrm{Pr1})\sim 6$, $\sigma_o(\mathrm{Pr1})/\sigma_o(\mathrm{Pr3})\approx 160$ is accompanied $T_g(\mathrm{Pr1})/T_g(\mathrm{Pr3})\sim 1.2$. Since the distribution of grain sizes is similar in all the Pr samples, it seems that σ_o depends on the grains' connectivity while T_g mainly on the grain sizes.

For several sintered and granular samples the resistivity measurements were extended above RT. Figure 3 shows $\sigma(T)$ for a sintered sample N3 (similar to N1) and a granular sample Pr5 (similar to Pr2) upon heating from 20 K to 450 K

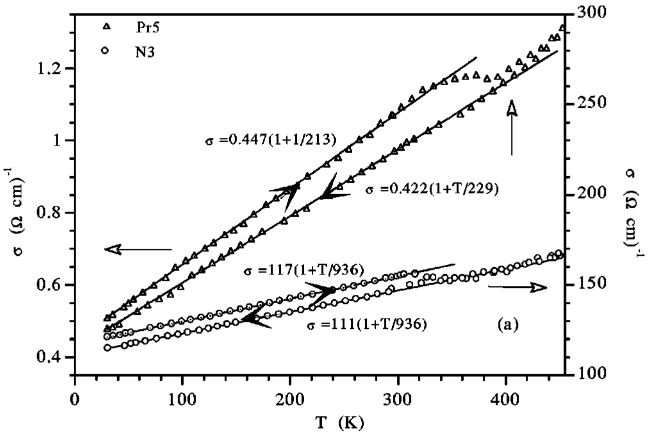

FIG. 3. σ vs T up to 450 K for a sintered sample N3 and a granular sample Pr5.

followed by cooling to 20 K. When T_c is approached from below, the $\sigma(T)$ plots deviate from the straight lines, their slopes drop and increase again above T_c. For $T > T_c$, $\sigma(T)$ is slightly superlinear. For both samples the $\sigma(T)$ plots are smoother upon cooling through T_c. Below RT the perfect linearity of the plots is restored; for both samples σ_o is slightly lower than its initial value, T_g(N3) remains unchanged, and T_g(Pr5) is slightly higher than before.

The absolute thermopower S, a property insensitive to the GB's,[19] was measured on the sintered sample N1 and on the granular sample Pr2 from liquid-He temperature to 450 K (shown in our Ref. 6). Up to RT, the negative, metalliclike values of $S(T)$ for these two samples are practically identical. The plots for both samples exhibit bends at 406 ± 0.5 K that mark T_c. This indicates that the electronic and magnetic properties of the bulk have not been affected by the mechanical treatment and that the different $\sigma(T)$ are caused by the different properties of the GB's.

Large deviations from Ohm's law could be obtained using pulsed currents applied to our most resistive samples. Here we present the results for sample Pr3. The bold symbols in the $\sigma(T)$ plot of Fig. 2 represent the temperatures for which detailed I-V measurements were carried out. The empty symbols represent the results of $\sigma(T)$ measured after the I-V measurements were completed. The two sets of data are identical for $T \geqslant 80$ K indicating that the prolonged exposure of the sample to high electric fields has not caused any damage to the sample or its contacts. Small differences (of less than 10%) are observed below 80 K; these are too small to be attributed to more than an instrumental error.

The J-E characteristics of Pr3 for various temperatures are shown in Fig. 4(a). The comparison between the J-E characteristics obtained at 10 K from dc and from pulsed measurements is shown in the inset to this figure. The two plots coincide at low fields, but above ~ 80 V/cm the dc $J(E)$ plot rises much faster due to Joule heating.

The $J(E)$ plots in Fig. 4(a) have been analyzed in terms of the FIT model.[10] In this model, the linear and nonlinear conductivities were derived for planar tunnel barriers of area A and width w with a potential V across them approximated by a parabolic function $V = V_o - 4V_o(x/w)^2$. As argued in

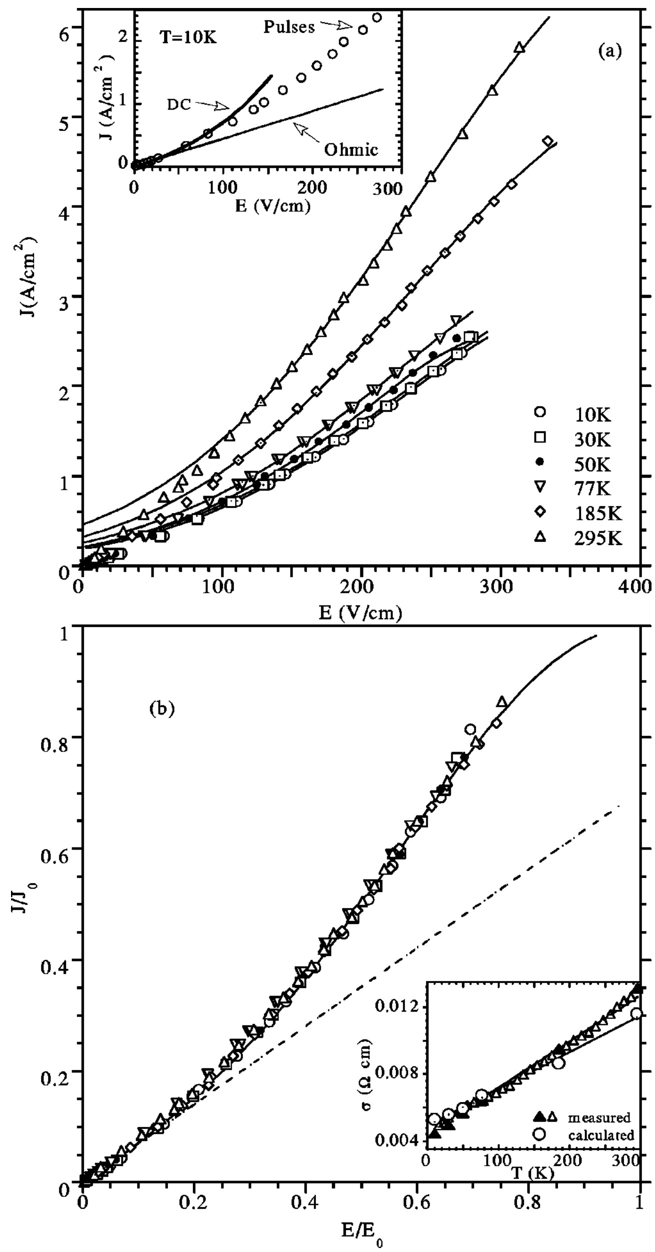

FIG. 4. (a) J-E characteristics of sample Pr3 for various T. Solid lines represent the $J(E)$ function of Eq. (1) fitted to the high-E range of the experimental data. Inset: Comparison of results for dc and pulsed currents. (b) J/J_o vs E/E_o using the fitted values of E_o and J_o from Table I. Solid line represents the modified $J(E)$ function for $a = 2.75$ and dashed line represents the ohmic limit of this function. Inset: Comparison between the measured and calculated σ.

Ref. 10, for reasonable distribution functions of the parameters, the behavior of a random resistor network is well described by single-junction characteristics. The forward current density J as a function of the applied electric field E is given by

$$J = J_o \exp\left\{ -a(T)\left[1 - \frac{E}{E_o}\right]^2 \right\}, \quad E < E_o, \tag{1}$$

TABLE I. Fitting parameters of Eq. (1) to the high-field range of the *J-E* characteristics of sample Pr3 at various temperatures.

T (K)	a	E_o(V/cm)	J_o(A/cm^2)
10	2.82	400	3.14
30	2.78	414	3.34
50	2.76	392	3.32
77	2.66	405	3.65
185	2.77	415	5.15
295	2.70	417	6.68
	2.75±0.06	407±10	

where J_o is a preexponential factor that contains all the weak temperature and field dependences of J, $E_o=4V_o/ew$ and $a=\pi\chi w/2$ $[\chi=(2mV_o/\hbar^2)^{1/2}]$ when tunneling is not affected by thermal fluctuations, otherwise a is a function of temperature.[10]

Since the backflow current is not included in Eq. (1), this equation is applicable for not too low fields. Also, the FIT Ohmic conductivity $[\sigma=\sigma_o\exp(-a)]$ cannot be derived from the zero-field limit of $dJ(E)/dE$.

According to Eq. (1), ln(J) vs E is a parabolic function. Parabolas were fitted to the data on such plots for $E>100$ V/cm with correlation coefficients $R^2>0.999$ (except for 77 K where the maximal R^2 was 0.9989 due to scattering of results). The fitting parameters a, E_o, and J_o are listed in Table I. Parameters a and E_o are practically independent of T. Their averages and standard deviations are given at the bottom of Table I. J_o rises quasilinearly with temperature at a rate close to that of the Ohmic conductivity.

Using fitted J_o and E_o, the normalized J/J_o-E/E_o characteristics were replotted in Fig. 4(b). The high-field as well as the low-field data for all T fall practically on the same curve. To simulate the Ohmic current density we added to $J(E)$ of Eq. (1) a backward current density $-J(-E)$. The solid curve represents the modified expression for the normalized current density. The average value of a (see Table I) was used in this calculation. It leads to $\sigma_{calc}=d[j(E)-j(-E)]/dE|_{E\to 0}=4aJ_o\exp(-a)/E_o$. In the inset of Fig. 4(b) we plotted calculated σ and replotted measured σ as functions of temperature. The two plots cross each other at around 100 K and the maximal deviations $(\sigma_{calc}-\sigma_{meas})/\sigma_{meas}$ are 0.19 at 10 K and −0.11 at 295 K. In view of the simplicity of this analysis, the agreement between the two sets of data is surprisingly good. It allows us to conclude that the temperature dependence of the conductivity is determined by the preexponent of the tunneling probability. From the values of a and E_o we may now estimate averages of the widths and the heights of the intergrain barriers for sample Pr3. Since bulk resistivity is negligible, the electric field at the grain boundary is $\sim d/w$ times larger than the measured E. Thus, the effective barrier height at a grain boundary is $V_o\sim(1/4)ewE_o(d/w)$. From Fig. 1(b), a rough estimate of d is 1 μm. Using the average E_o found above we obtain $V_o\approx 10$ meV. The expression for the average width of the barriers is $w=(2a/\pi)\sqrt{\hbar^2/(2mV_o)}$. Using the average value of a and the free-electron mass we obtain $w\approx 30$ Å. The effect of thermal fluctuations on intergrain tunneling is important when the electrical energy stored in the capacitor (at the GB) is much larger than k_BT. Since fluctuations are negligible in our case, we obtain a low limit for the area A of the typical junction. Using the data calculated above, $k_BT=1/40$ eV and the dielectric constant $\epsilon=1$, we obtain $A\gg 10^3$ nm^2 which seems reasonable for grains of ~1 μm diameter.

The preexponent depends on the densities of states on both sides of the GB's along the conduction path. These depend on the local magnetizations and their relative orientation. In the absence of an applied magnetic field the orientations of the grains' magnetizations are random for all temperatures and the corresponding $\langle\cos^2\theta/2\rangle$ term in the preexponent is regarded as constant. On the other hand, the magnetization at the interface may be different from that of the bulk of the ferrimagnetic grain; its magnitude and orientation as functions of temperature may depend on the intergrain medium.[20] This would allow for a non-negligible temperature dependence of the $\langle\cos^2\theta/2\rangle$ term. However, above the hysteretic temperature range around T_c, σ continues to rise with temperature at a rate similar to that below RT, indicating that the T dependence of the preexponent (of σ) may be of different origin. Measurements of $\sigma(T)$ extended to much higher temperatures could help in reaching a firmer conclusion but these are not feasible at the present.

One of the main assumptions of the FIT model is that the behavior of a random resistor network is well described by single-junction characteristics. It would be very interesting to measure the temperature and electric-field dependence of the conductance of individual GB's in SFMO as carried out in a manganite.[21]

IV. SUMMARY

In the absence of an applied magnetic field, the intergrain tunneling conductivity in SFMO may be expressed as $\sigma=\sigma_o(1+T/T_g)$ up to temperatures close to T_c. Around T_c, σ is hysteretic and above T_c it increases with T at a rate similar to that below RT with a slight tendency towards superlinear dependence on T.

In the course of this research we have been attracted by the FIT model since it could provide a very simple and intuitive explanation to our findings. This model extends from elastic tunneling (that is independent on temperature) to activated hopping; for a range of parameters $\sigma(T)$ may increase linearly with T over wide ranges of temperatures. In this case, the linear dependence of σ is governed mainly by the exponent of the tunneling probability.

In order to identify which of the tunneling parameters, the exponent or the preexponent, is responsible for the linear temperature dependence, the transport measurements on granular SFMO were extended to the nonlinear (electric-field-dependent) conductivity regime using high current pulses. The analysis of the results in terms of the theoretical *J-E* characteristic included in the FIT model[10] leads to a result that was fairly surprising for us. It indicated that the preexponent of the tunneling probability increases linearly with temperature while the parameters in its exponent are practically independent of T.

The parameter in the preexponent responsible for a linear temperature dependence has not yet been identified. The remarkably simple temperature dependence of intergranular conductivity in SFMO remains puzzling. An important contribution towards understanding this behavior would be the results of transport measurements carried out on single GB's.

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[12] The FIT model predicts $\sigma \propto \exp(-a)$, where $a=(T_1/T_o)/(1+T/T_o)$.

[13] For $2.5 \leqslant T_1/T_o \leqslant 3$ and $0 \leqslant T/T_o \leqslant 0.9$, the expression $\exp(-a)$ (see Ref. 12) increases linearly with T/T_o by more than a factor of 3 $(R^2 \geqslant 0.9997)$. The expression $a\exp(-a)$ with $T_1/T_o \approx 4.5$ exhibits a similar linearity for a narrower range of T/T_o.

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