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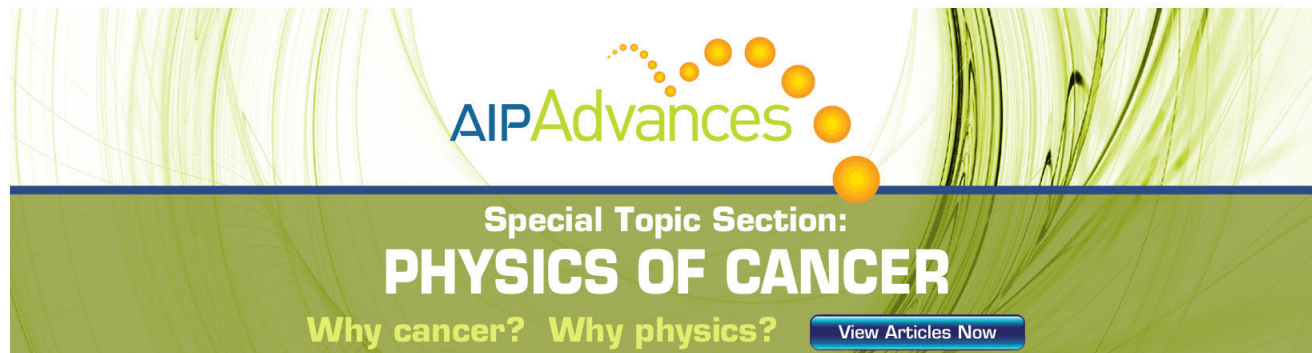Journal Homepage: http://jap.aip.org/

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Anneal-tunable Curie temperature and transport of La$_{0.67}$Ca$_{0.33}$MnO$_3$

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Resistivity measurements on a La$_{0.67}$Ca$_{0.33}$MnO$_3$ film are reported for a series of argon anneals at successively higher temperatures. T_c, the ferromagnetic ordering temperature, increases uniformly with increasing annealing temperature and annealing time. Hence, T_c can be tuned by appropriate annealing. In order to fully anneal these samples, i.e., achieve bulk properties, it proves sufficient to anneal them in argon. Further annealing in oxygen produces only minor changes in the resistivity. Data from T_c up to 1200 K show activated conduction with $\rho = BTe^{E_a/kT}$, the temperature dependence predicted by the Emin–Holstein theory of adiabatic polaron hopping. Their model fits both data from the partially annealed and fully annealed samples better than the variable range hopping or semiconductor models which have been used by previous workers. The activation energy E_a and resistivity coefficient B decrease with increasing maximum anneal temperature. These changes, together with the increase in T_c, are consistent with an anneal induced relaxation of the Mn–O–Mn bond angle. The time dependent resistivity during annealing at a fixed temperature follows the equation $\rho = \rho_0\{1 - D \ln[1 + (t - t_0)/\tau]\}$, making it possible to acquire data in a reversible regime, and also to obtain an estimate of the annealing activation energy. © *1996 American Institute of Physics.* [S0021-8979(96)06120-8]

I. INTRODUCTION

Recent interest in La$_{0.67}$Ca$_{0.33}$MnO$_3$ has focused on its colossal magnetoresistance (CMR), with the implicit hope that this feature could be technologically useful. The largest magnetoresistance is found near T_c,[1] therefore, CMR applications would require T_c to be close to room temperature, or above. In this study, we report measurements of the resistivity maximum, T_{MI} (metal–insulator), which in fully annealed samples is equal to the ferromagnetic ordering temperature T_c.[1] In this work, we-make the reasonable assumption that in the partially annealed state T_{MI} is approximately equal to T_c. Previous work has demonstrated that samples grown with the same composition, but at different substrate temperatures, can have different values of T_{MI}.[2] This paper shows how annealing (in argon) can be used to systematically change the conductivity of a sample, and thus tune T_{MI}.

Three different models have been suggested to explain the conduction mechanism above T_{MI}. Each predicts a different temperature dependence of the resistivity. Variable range hopping (VRH) has been suggested by several authors to explain conduction at temperatures above T_{MI} using the formula $\rho = Ce^{(T_0/T)^{1/4}}$.[3,4] Other authors have invoked the semiconductor formula $\rho = Ce^{E_g/2kT}$, either with a constant energy gap, or a band gap with a temperature dependence.[5] The last models we will consider are small polaron hopping.[1] In this case, the polaron can be thought of as trapped inside a local energy well of height E_a. In the presence of an applied electric field, one side of the well is lowered slightly with respect to the other. This makes the polaron more likely to hop in that direction. Here we must distinguish between two cases. In the nonadiabatic approximation, the polaron is assumed to have a small probability of making a jump during each attempt period, and Holstein finds $\rho = CT^{3/2}e^{E_a/kT}$.[6] In the adiabatic approximation, the polaron has a high probability of jumping into the next site, and it is assumed that the polaron makes several jumps back and forth before the phonon wave recedes. This case was considered by Emin and Holstein in 1969, and gives $\rho = BTe^{E_a/kT}$.[7] It is this latter case that best fits the data. Furthermore, adiabatic polaron hopping is observed in both the partially annealed and fully annealed samples.

II. EXPERIMENT

A 1500 Å epitaxial film grown by metal organic chemical vapor deposition on LaAlO$_3$[8] was chosen for this study. The film was grown at 45 Å per minute at a susceptor temperature of 600 °C (the surface temperature of the substrate was approximately 470–500 °C) with an oxygen partial pressure of 3.75 Torr. The sample was then cooled below 100 °C in this same atmosphere. In previous work similarly grown annealed films reproducibly exhibited a large magnetoresistance, and a resistivity of the form $\rho = BTe^{E_a/kT}$ above T_{MI}. Furthermore, such films exhibited the same properties as bulk La$_{0.67}$Ca$_{0.33}$MnO$_3$.[1] Therefore, in this study we expect the behavior of the selected film, once fully annealed, to be representative of the bulk material.

Platinum leads were attached to the sample with a small amount of silver epoxy. A type K thermocouple was used as a thermometer. Four point dc Van der Pauw[9] resistance measurements were carried out in the Ohmic regime with currents ranging from 0.01 μA to 0.1 mA. Offset voltages were subtracted by reversing the current. At each data point, five measurements were averaged, resulting in errors of less than 1%. The sample was heated in a furnace with a controlled
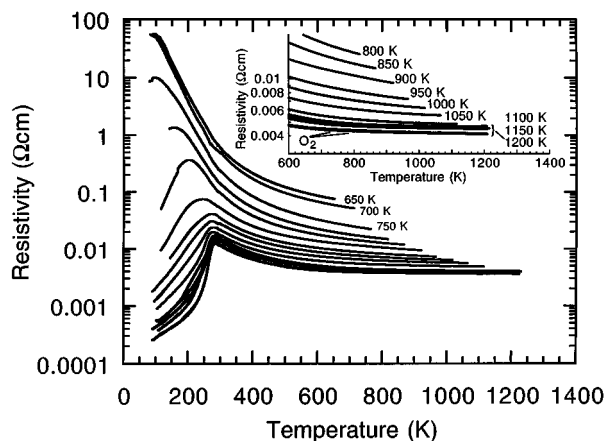
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FIG. 1. Resistivity on cooling after successive annealing in argon. The first run is the upper curve. T_h, the temperature at which the sample was held for 10 h, is labeled to the right of each curve. The last two runs (bottom two curves) were annealed in oxygen; note that this had little effect on the sample. Inset, same data plotted on a larger resistivity scale for clarity.
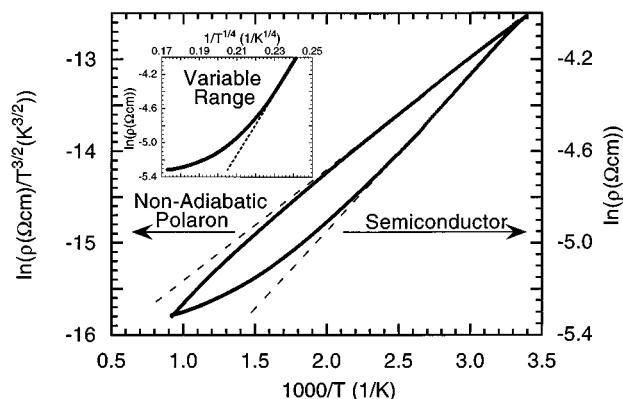

FIG. 2. The variable range hopping, semiconduction, and nonadiabatic polaron hopping models do not fit the data over any appreciable temperature range. For clarity, only the T_h=1100 K data are plotted.

atmosphere from 295 up to 1200 K, and cooled in an open dewar of liquid nitrogen from 80 to 295 K, with care taken to minimize the effect of water contamination.[10] All annealing was done in flowing argon, with an average oxygen sensor reading of 600 ppm. The sample was heated and cooled at 2 K per minute.

The sample was first heated to a hold temperature of T_h=650 K, maintained at that temperature and then cooled to 80 K. This was repeated 11 times, each time increasing T_h by 50 K. In each cycle, the sample was held at T_h for 6–10 h. The sample was cycled three more times at T_h=1200 K; the last of these runs showed no change in the resistance from the previous run. The sample was then annealed twice in 100% oxygen, and then a final time in argon, all again held for 10 h at T_h=1200 K. The measurements reported here were taken as the sample cooled, since the sample's resistance changed with time, when heated above the highest temperature to which it had previously been exposed. Changes in resistivity, at a fixed temperature, occurred on a logarithmic time scale (see Fig. 6). Hence, after holding at T_h for 10 h, the relaxation time after cooling by 100 K was large enough to consider the remainder of the cooling process as almost reversible.

III. RESULTS AND DISCUSSION

In Fig. 1 the resistivity is plotted versus temperature for the cooling part of each annealing cycle. The data from the film after the first anneal (T_h=650 K) is the upper curve. For clarity, the heating curves have not been plotted, however, the heating curve for T_h is, to good approximation, given by the cooling curve for T_h-50 K. With each anneal, T_{MI} increases and the resistance decreases.

It is important to note that no oxygen was present during the first set of anneal cycles, and yet T_{MI} still increases. It has been suggested that T_{MI} increases with higher oxygen content in $La_{0.67}Ca_{0.33}MnO_{3+\delta}$.[11] However, our data suggest that T_{MI}, increases as δ stays constant (or decreases slightly). The last two curves at the bottom of Fig. 1 are the result of

anneals in 100% oxygen. T_{MI} does not change appreciably with these last anneals. A final anneal in argon also had little effect. It is clear that annealing in oxygen is not a requirement to fully anneal this sample.

Figure 2 shows the inability to agree with the data of the three models of conduction which have been considered by others. The theoretical curve for each model is shown as a dashed line. It should be noted however, that immediately above T_{MI}, and on a sufficiently small temperature scale, all of these models fit the data well. A straight line fitted to these curves yields R=.9648 for VRH, R=.9909 for semiconduction, and R=.9990 for nonadiabatic small polaron hopping, where R is the linear correlation coefficient. In these plots, for clarity, only the data for T_h=1100 K are shown.

Figure 3 shows all of the high temperature data plotted as $\ln(\rho/T)$ versus $1/T$. A straight line fitted to these curves has $R \sim .99990$, in strong support of the adiabatic small polaron hopping model. Figure 3 also allows the activation energy E_a and the resistivity coefficient B from the formula $\rho = BTe^{E_a/kT}$ to be calculated for each cycle. These data are summarized in Table I. Figure 4 shows how E_a and T_{MI}
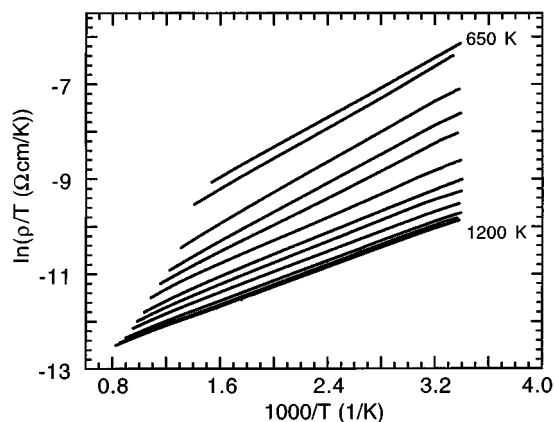

FIG. 3. The adiabatic small polaron hopping model fits the data well at all stages of annealing. Each line is the cooling curve after being held at T_h for 10 h. T_h=650 K for the top curve, and increases by 50 K for each successive run, up to T_h=1200 K for the bottom curve. The data for successive runs at T_h=1200 K, including the two oxygen runs, are not plotted here.

TABLE I. Parameters as measured on cooling after being held at T_h for 10 h (* runs were annealed for 6 h). The activation energy E_a and resistivity coefficient B are from the adiabatic small polaron hopping expression $\rho = BT \exp(E_a/kT)$. T_{MI} is the resistivity maximum. The first 15 runs were annealed in argon.

Run	T_h (K)	E_a (eV)	T_{MI} (K)	B (10^{-6} Ω cm/K)
1*	650	0.136	78	10.60
2*	700	0.139	78	7.78
3*	750	0.139	96	3.76
4	800	0.132	155	2.89
5	850	0.124	203	2.69
6	900	0.106	245	2.97
7	950	0.101	273	2.35
8	1000	0.098	273	2.13
9	1050	0.093	275	2.00
10	1100	0.092	274	1.73
11	1150	0.091	275	1.63
12	1200	0.089	274	1.60
13	1200	0.087	274	1.62
14	1200	0.086	273	1.66
15	1200	0.086	274	1.69
16 (Oxygen)	1200	0.083	271	1.56
17 (Oxygen)	1200	0.083	274	1.56

FIG. 5. The resistivity coefficient B in $\rho = BTe^{E_a/kT}$ depends on the number density n through $B = 2k/3ne^2a^2v$. The peak around 850 K is where E_a and T_{MI} are rapidly changing and is not believed to be significant.

change with increasing T_h. E_a decreases with increasing T_h, implying that the energy barriers to the polaron's motion are thermally settling. T_{MI} rises linearly as the anneal hold temperature is increased, and then levels off at the "fully annealed" value $T_{MI} = 274$ K. Hence T_{MI}, for $La_{0.67}Ca_{0.33}MnO_3$, may be tuned to any given temperature between 80 and 274 K by appropriate annealing.

Figure 5 shows the change in B, the resistivity coefficient. According to Emin and Holstein, $B = 2k/3ne^2a^2v$.[7] Here, k is Boltzmann's constant, e is the electronic charge, n is the number density of charge carriers, a is the site-to-site hopping distance, and v is the longitudinal optical phonon frequency. It seems unlikely that a or v changes sufficiently with annealing to account for the large decrease in B. However, it is possible that B decreases due to an increase in n.[12] This could be the result of an ordered phase, containing electrons which can contribute to conduction, mixed in with a

disordered phase, whose electrons face activation energies too large to hop over. As the disordered phase slowly becomes ordered upon annealing, the effective number density of electrons increases. After sufficient annealing, the effective number density of electrons should equal the total number density of conduction electrons, $n = 5.6 \times 10^{21}$ cm^{-3}, corresponding to the doping level of .33 carriers per cell. In the absence of a value for the longitudinal optical phonon frequency of $La_{0.67}Ca_{0.33}MnO_3$ in the literature, we have calculated $v = 2.7 \times 10^{13}$ Hz, for $a = 3.9$ Å and the number density given above. This is of the same order of magnitude as the frequencies of phonon peaks in optical conductivity data taken for $La_{.825}Sr_{.175}MnO_3$.[13] Using these parameters, Fig. 5 shows how n increases with increasing T_h.

It is interesting to note that T_{MI} reaches its fully annealed value when $T_h = 950$ K, yet B and E_a continue to decrease long after. Table I shows the changes in E_a, T_{MI} and B after successive runs, the final six all at $T_h = 1200$ K. The two final runs were done in 100% oxygen. E_a continues to change until about the fourteenth run, while T_{MI} reaches its "fully annealed" value after only the seventh run. Furthermore, only B and E_a change somewhat upon annealing in oxygen. Table I shows that T_{MI} remains roughly unchanged for the last eleven runs, whereas B and E_a drop noticeably after the first oxygen anneal, and then remain constant.

The main experimental conclusions made so far in this article are that as the sample is annealed, T_{MI} increases, and, in the adiabatic small polaron model, E_a and B decrease. For the remainder of this article, we will speculate on a possible mechanism for these changes.

Recent experiments have shown that T_c[14] and E_a[4] (interpreted as T_0 in the VRH model) depend on the Mn–O–Mn bond angle, as determined by controlling the average radius of the A-site atom in $AMnO_3$ while keeping the dopant concentration constant. If we assume that annealing reduces local disorder, then we can explain all of our data from the assumption that T_c, E_a, and B depend on the Mn–O–Mn bond angle. This assumption is reasonable in view of the result, as noted in,[14] that the Néel temperature in the superexchange system $RFeO_3$, where R is a rare earth element, is sensitively dependent on the Fe–O–Fe bond
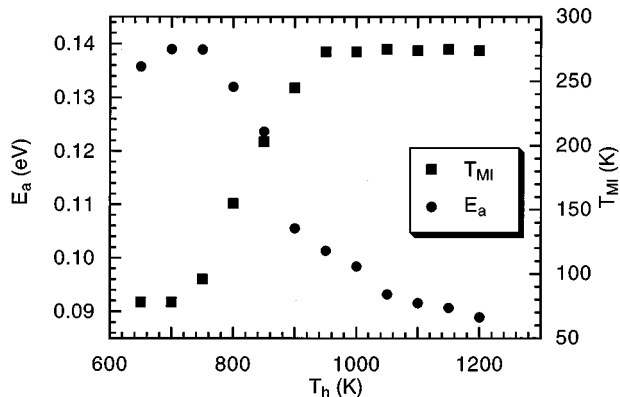

FIG. 4. The activation energy E_a, as calculated from Emin and Holstein's formula $\rho = BTe^{E_a/kT}$, and the temperature at which the resistance is a maximum T_{MI}, are plotted as a function of the hold temperature. T_{MI} reaches the fully annealed value of 274 K after seven runs, whereas E_a continues to decrease well after (see Table I).
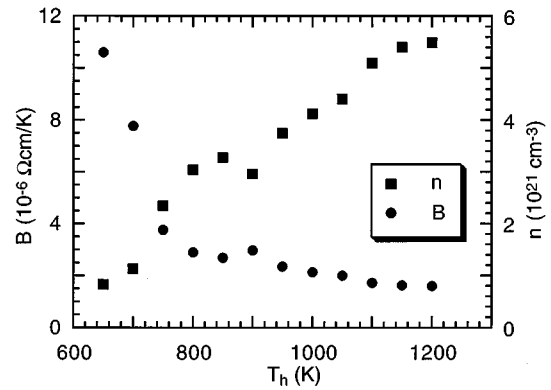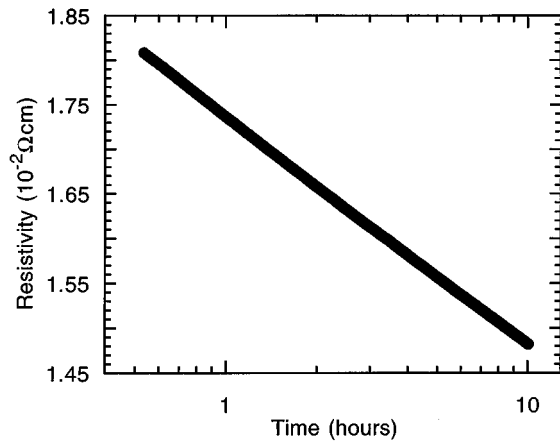
FIG. 6. At a fixed hold temperature (T_h=800 K shown here) the resistivity decreases logarithmically according to the formula $\rho=\rho_0\{1-kT_hU\ln[1+(t-t_0)/\tau]\}$ with U, the activation energy for annealing, equal to roughly 1 eV.

angle.[15] Since T_c depends on the magnetic coupling between ions, it is plausible that a distorted Mn–O–Mn bond angle results in a lower T_c, and that as the angle relaxes, the coupling and hence T_c increase. Furthermore, since a distorted bond angle means a disordered lattice and hence a higher energy barrier for the polaron to hop over, one may expect distorted bonds to contribute to higher activation energies. Also, since B is inversely proportional to the number density of carriers, and electrons associated with distorted bonds are likely to be localized, one would expect distorted bonds to result in larger resistivity coefficients. Furthermore, as the sample is annealed in argon the bond angle thermally settles into its unstressed orientation, thus lowering E_a and B, and increasing T_c. However, a relatively small number of oxygen deficient sites, with their maximally deformed bond angle, contribute to higher-than-equilibrium values for B and E_a. This does not substantially affect T_{MI}, since T_{MI} saturates earlier in the annealing process, indicating that T_c is less dependent on the bond angle than the activation energy and resistivity coefficient. After oxygen is forced into the sample the bond angles in the oxygen deficient sites return to normal, giving the drops in B and E_a after the first oxygen anneal. This viewpoint is further supported by the fact that subsequent oxygen and argon anneals had no effect on B and E_a.

The result $\rho=BTe^{E_a/kT}$ was derived for a single value of the activation energy E_a. We have numerically investigated the case of a gaussian distribution of activation energies, and found that, even if present with a fairly wide distribution, it would be difficult to observe experimentally. However, such a distribution could account for both the lack of a minimum at $T=E_a/k$ in the curves shown in Fig. 1, and the very slight negative curvature observable in the curves shown in Fig. 3.

Resistance as a function of time during the hold at a constant T_h is plotted in Fig. 6, for T_h=800 K. Similar curves for each value of T_h can be fitted very well to $\rho=\rho_0\{1-D\ln[1+(t-t_0)/\tau]\}$. It is not possible to fit these curves to a diffusion type equation with a $\sqrt{t}$ dependence, nor

to an exponential time dependence. Values of τ vary from 300 s for the first anneal to 10^4 s for the final anneals. This sets the time scale for the relaxation of the Mn–O–Mn bond angle, and for other ionic motion. We can extract an activation energy for these processes from $D=kT_h/U$, by plotting D versus, T_h for each value of T_h. Such a plot gives D roughly proportional to T_h, with a value of $U\approx1$ eV. This is a typical value for activation energies in atomic processes.[16] Careful examination of the curve in Fig. 6 shows that the decay of the resistivity is actually less than logarithmic. This indicates that D depends on $\rho-\rho_{eq}$, where ρ_{eq} is the fully annealed value of ρ, and hence that the resistivity will not decrease indefinitely. This is expected since the Mn–O–Mn bond angle will eventually reach its equilibrium value.

IV. CONCLUSION

In conclusion, we have shown that oxygen is not required to anneal these films. Furthermore, above T_{MI}, the resistivity of both partially and fully annealed samples obeys $\rho=BT\exp(E_a/kT)$, as predicted by adiabatic small polaron hopping. Hence, the conduction mechanism does not change with T_{MI}. In principle, T_{MI} may be tuned by appropriate annealing. The changes in T_{MI}, E_a, and B have been shown to be consistent with an anneal induced relaxation of the Mn–O–Mn bond angle.

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