MISSOURI S&T

Missouri University of Science and Technology

Scholars' Mine

Materials Science and Engineering Faculty Research & Creative Works

Materials Science and Engineering

01 Sep 1990

Evidence for a Crossover from Multiple Trapping to Percolation in the High-Temperature Electrical Conductivity of Mn-doped LaCroO₃

Ryne P. Raffaelle

Harlan U. Anderson
Missouri University of Science and Technology, harlanua@mst.edu

Don M. Sparlin
Missouri University of Science and Technology, sparlin@mst.edu

Paul Ernest Parris
Missouri University of Science and Technology, parris@mst.edu

Recommended Citation

Evidence for a Crossover from Multiple Trapping to Percolation in the High-Temperature Electrical Conductivity of Mn-Doped LaCrO₃

R. Raffaelle, H. U. Anderson, D. M. Sparlin, and P. E. Parris

Departments of Physics and Ceramic Engineering, University of Missouri-Rolla, Rolla, Missouri 65401

(Received 5 June 1990)

We explain the deep electrical conductivity minimum near $x = 0.05$ in the perovskite-type ceramic $LaCr_{1-x}Mn_xO_3$ as a crossover between two different regimes of hopping conduction. At low Mn concentrations the diffusion of small polarons among Cr ions is limited by multiple trapping at energetically lower Mn sites. At higher concentrations a percolating path of Mn sites forms and direct transport between Mn ions dominates the conduction process.

Interest in thermoelectric materials and electrical components capable of operating at very high temperatures has led to considerable study into the electrical properties of conducting ceramics, examples of which include metallic oxides possessing the perovskite structure ABO_3. In addition, the search for materials possessing the structural stability and electrical conductivity required in fuel-cell environments has led to the investigation of *substitutionally mixed* systems, whose end members possess material properties desired in the composite.[1-3] Recently studied examples include the series $Y(Cr,Mn)O_3$ and $La(Cr,Mn)O_3$. In both of these materials, Mn substitutes for Cr in the B site of the perovskite structure and the electrical conductivity of the end members occurs through the hopping of p-type small polarons among the Mn or Cr site cations.[1] The mixed systems, however, can have properties considerably different than those of either of the end members. For example, the substitutional inclusion of a small amount of the ion associated with the more conductive end member leads to a conductivity which drops orders of magnitude below that which occurs for either end member of the series.[2,3]

Based upon a detailed experimental study of the electrical conductivity of the $La(Cr,Mn)O_3$ series, we offer in this Letter an explanation for the conductivity minimum that occurs in these systems. Specifically, we propose that the observed minimum represents a crossover between two distinct conduction mechanisms. These mechanisms have traditionally been characterized by two separate theoretical models of hopping transport in disordered systems: the random-well model and the random-barrier model. The random-well model is an exactly soluble transport model which has proven useful for understanding the hopping diffusion of particles among energetically different sites, and in particular for understanding the regime of *trap-limited* diffusion in which transport is dominated by a small concentration of "deep wells" out of which the hopping rate is very low.[4,5] The random-barrier model has proven useful in describing hopping transport among degenerate sites which are

separated from one another by symmetric barriers of random height.[4,6] It is perhaps best known in the limit in which there are two types of barriers separating sites: finite barriers associated with a nonzero hopping rate, and infinite or blocking barriers over which hopping cannot occur. A two-barrier model of this type with varying concentrations of finite and infinite barriers describes conduction on a percolating lattice.[6] The conductivity of the $La(Cr,Mn)O_3$ series displays behavior which contains key aspects of both of these models and stems, as we explain below, from the existence of a significantly lower polaron energy at the sites at which Mn ions have been substituted for Cr ions. This first observation of a clear crossover between these two limits of standard transport theory underscores what we believe to be a need for the development of a unified model of hopping transport in binary systems, which is more general than that contained in either the random-well model or the random-barrier model alone.

To ensure adequate data for analyzing the compositional dependence of the conductivity, samples of the series $LaCr_{1-x}Mn_xO_3$ containing concentrations of Mn in 10% increments were prepared using methods described in Ref. 3. Additional samples were produced in 5% increments in the region associated with the conduction minimum. The conductivity as a function of temperature was then determined using a four-point-probe technique. Results are presented in Figs. 1 and 2.

At the high temperatures relevant to this study, the mobility of small polarons in a pure material is proportional to the rate[7]

$$W = J^2(\pi/4E_a kT)^{1/2}\exp(-E_a/kT) \qquad (1)$$

for hopping between degenerate neighboring polaron sites. In (1), J is the nearest-neighbor electron-transfer-matrix element, and the small-polaron activation energy E_a is related to the lattice relaxation energy E_r associated with the formation of the small polaron. At a finite fractional concentration c of small polarons the hopping rate is reduced due to site blocking, i.e., the possibility that the neighboring site may already be occupied by a
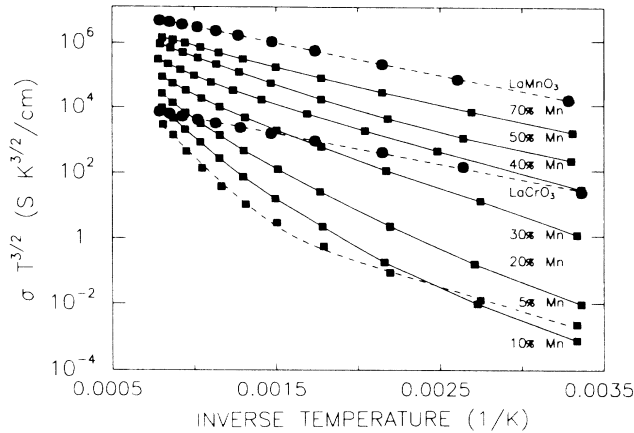
FIG. 1. Logarithmic plot of $\sigma T^{3/2}$ as a function of inverse temperature for the series La(Cr,Mn)O_3. Circles represent end members and squares represent mixed samples. Dashed lines are theoretical fits to the data.

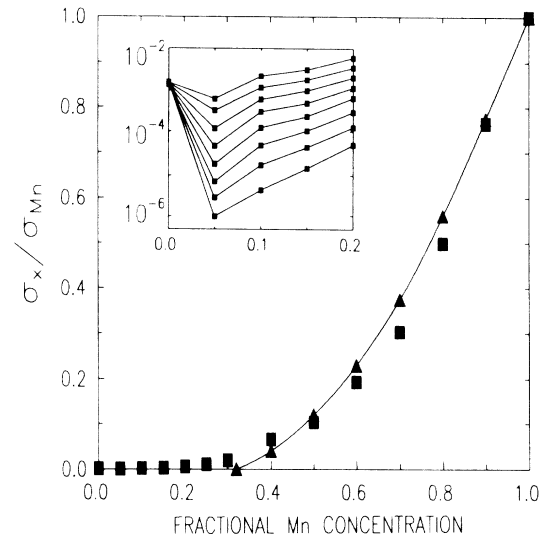FIG. 2. Normalized conductivity vs Mn content in La(Cr, Mn)O_3. Squares represent measured data at 1273 K and triangles represent site-percolation data from Ref. 6. Inset: Logarithmic plot of the normalized conductivity as a function of Mn content in the crossover regime for temperatures in the range 573 (lowermost curve) to 1273 K in increments of 100 K.

charge carrier. In the simplest approximation this has the effect of reducing the mobility $\mu = (1-c)eWa^2/kT$ by a factor of $1-c$ from what it would be in the dilute limit.[8] For a low, but temperature-independent small-polaron concentration $p = c/\Omega$, where Ω is the unit-cell volume, the conductivity $\sigma = pe\mu$ should be thermally activated with an algebraic $T^{-3/2}$ prefactor, and the product $\sigma T^{3/2}$ should exhibit a straight line when plotted on a logarithmic scale as a function of the inverse temperature. The end members of the series, LaCrO$_3$ and La-MnO$_3$, exhibit this behavior over a wide temperature range (see Fig. 1) and have very similar activation energies. The conductivity of pure LaMnO$_3$ is ~600 times greater than that of LaCrO$_3$. A least-squares fit to the data (shown as the upper two dashed lines in Fig. 1) gives an activation energy of 182 ± 2 meV for LaCrO$_3$ and 194 ± 1 meV for LaMnO$_3$. The linearity of the data for the end members over such an extended temperature range is consistent with the earlier identification of the conductivity in these materials as being due to a temperature-independent concentration of p-type small polarons.[1-3]

In spite of the larger intrinsic conductivity of La-MnO$_3$, a small substitution of Mn for Cr in LaCrO$_3$ results in a sharp drop in the room-temperature conductivity from that exhibited by either end member (see Fig. 1 and the inset in Fig. 2). This minimum, which at room temperature is more than 4 orders of magnitude below that of pure LaCrO$_3$ occurs at a Mn concentration around (5-10)%. In addition, these small substitutions of Mn result in a nonlinear reciprocal-temperature dependence with increased slope. The maximum slope observed occurs in the 5%-Mn sample at high temperatures and corresponds to an activation energy of 1.1 ± 0.1 eV.

We have associated this limiting slope with the energy ε required for a small polaron at a Mn site to make a hop

to a neighboring Cr site. This energy would have two primary contributions: one related to the lattice relaxation energy E_r and another from the energy difference $\Delta E = E_{Cr} - E_{Mn}$ between a polaron on a Cr site and on a Mn site. Assuming the contribution from E_r to be of the same order of magnitude as that of the end member in these and other perovskites,[8] ~100-300 meV, we can estimate the difference in site energies to be in the range $\Delta E \sim 700$-900 meV. Such a relatively large difference in site energies implies that a small concentration of energetically lower Mn sites will act as traps for polarons migrating among the Cr ions. A complete description of the conduction process in this system should then involve four nearest-neighbor hopping rates: $W_{c,m}$, $W_{m,c}$, $W_{m,m}$, and $W_{c,c}$, in which $W_{c,m}$ represents the intrinsic hopping rate from a Cr site to a neighboring Mn site, and similarly for the rest. The rate and activation energy for hops between adjacent Cr sites have no particular relation to the rate for hops between Mn sites (although as the end members show, the corresponding activation energies appear to be quite similar in this series). Detailed-balance considerations stemming from the requirement that the system achieve thermal equilibrium would require that forward and backward hopping rates between sites differing in energy by an amount ΔE be related to one another through a Boltzmann factor, i.e., $W_{m,c}/W_{c,m} \sim \exp(-\Delta E/kT)$. Thus, in the temperature range considered, we would expect the rate for hopping out of a Mn site and onto a neighboring Cr site to be exponentially smaller than the rate associated with the re-

verse jump or with the rate for jumping between adjacent pairs of similar sites.

Thus, in the small-x limit, a single polaron migrating on the predominantly Cr sublattice will make a transition into an isolated energetically lower Mn site. A comparably large amount of time, $\tau \sim 1/W_{m,c}$, must then elapse before the polaron can hop back onto a neighboring Cr site, from which it can continue its migration through the crystal. In the theory of disordered systems this type of transport is referred to as "multiple trapping" or "trap-limited diffusion," and has been shown to lead to a conductivity which is dominated by the slower rate for leaving the energetically lower state.[4,5] This trap-limited picture is expected to apply in the small-x limit, wherein the rate out of the Mn sites is almost always given by the Mn-to-Cr hopping rate (so that the contribution from Mn-Mn nearest neighbors is negligible). Thus, its applicability is primarily limited to the 5%-Mn sample, which does, in fact, display the steeply activated behavior which we have attributed to multiple trapping.

At low temperatures the conductivity of the 5% sample displays a limiting slope closer to that of LaCrO$_3$. This suggests that for $x = 0.05$ there is a slightly greater number of polarons in the crystal than there are Mn traps. As the temperature decreases, most of the Mn sites become filled with carriers and the number of effective (i.e., unoccupied) trap sites approaches zero. The excess (untrapped) carriers can then travel a much greater distance among Cr sites before encountering an unoccupied trap. In this limit the rate for hops among adjacent Cr sites plays a more important role in determining the conductivity. At higher temperatures there is a greater probability that any given trap encountered in the crystal will be unoccupied, and thus the role of the detrapping rate $W_{m,c}$ dominates the conduction process.

To quantitatively test this trap-limited picture of conduction for the 5% sample we need to modify the usual binary random-well model to include the effects of site blocking by other carriers. Thus, we consider a random distribution of sites with two different energies E_1 and E_2 (separated by an amount ΔE), in fractional concentrations x and $1 - x$, respectively, on which a total fractional concentration c of carriers are distributed in thermal equilibrium according to the Fermi distribution function $f(E,T)$. By considering the diffusion constant of a "tagged" particle migrating in this random trapping environment (which contains a fractional concentration $q = x[1 - f(E_2,T)]$ of unblocked "deep wells") we obtain, taking $x = 0.05$, $c = 0.0505$, and $\Delta E = 0.7$ eV, the lower dashed curve in Fig. 1. In this curve, the hopping rate out of the higher-energy Cr sites has been taken from the fit to the pure LaCrO$_3$ data, while the hopping rate out of the lower-energy Mn sites has been chosen to give the high-temperature slope seen in the 5% sample. The quantitative agreement with the data supports our

interpretation of the conduction mechanism in this regime as being due to multiple trapping.

As the Mn concentration is increased a connected path of Mn sites spanning the crystal will eventually form. Once this occurs, particles trapped in an extended cluster of Mn traps will no longer need to make a transition to a Cr site in order to participate in conduction. Hence, the conductivity will no longer be limited by the slow rate $W_{m,c}$, and the trap-limited picture will no longer apply. Instead, conduction should cross over to a percolative regime[6] characterized by a conductivity which increases with Mn concentration, and an activation energy which approaches that associated with the rate $W_{m,m}$ (that of the end member LaMnO$_3$). Under the assumption that the substituted Mn ions randomly occupy Cr sites in the cubic B-site sublattice, a large increase in conductivity should occur in the vicinity of the critical concentration $x_c \sim 0.31$ for site percolation in a cubic lattice.[6]

The conduction data exhibit this behavior (see Fig. 1). There is a large increase in conductivity for $x \sim 0.30$, and the temperature dependence for samples with $x > 0.30$ is characterized by a slope which becomes progressively closer to that of the end member as x increases. The increase in slope at higher temperatures is evidently due to the ability of carriers to occasionally pass through the energetically higher Cr sites, rather than having to go around them as would be required if the carriers were strictly confined to Mn sites. To facilitate comparison, a linear plot of conductivity as a function of Mn composition at 1273 K is presented in Fig. 2, along with Kirkpatrick's simulation data for the site-percolation model taken from Ref. 6. The agreement of the measured data with the percolation model is quite reasonable, particularly when one considers that there is expected to be a slight dependence in the small-polaron concentration on Mn composition.

Thus, the conductivity minimum observed in these materials as a function of increasing Mn content is consistent with a crossover from a multiple-trapping regime at low Mn concentrations (in which the conductivity decreases with increasing Mn content) to a percolative regime (in which the conductivity increases with increasing Mn content). In the crossover region $0.1 > x > 0.3$ the conductivity increases with x for several possible reasons. The small-polaron concentration may simply be increasing with Mn content in this region, in which case a strictly nearest-neighbor model may suffice for analyzing the crossover. Alternatively, if any of the greater-than-nearest-neighbor Mn-to-Mn hopping rates are significantly larger than the nearest-neighbor Mn-to-Cr rate, the increase could reflect the diminishing separation distance between isolated Mn sites and, possibly, a percolation transition of greater-than-nearest Mn neighbors.[9] Neither of these alternatives affect our interpretation of the large-x (> 0.3) and small-x (~ 0.05) regimes, but it does emphasize the need for a unified theory of hopping

transport in binary systems which is capable of handling the crossover region.

In summary, we have shown that a picture involving small-polaron hopping between Cr and energetically lower Mn sites is consistent with the observed electrical conductivity in the $La(Cr,Mn)O_3$ series. A suitable modification of the binary random-well model quantitatively describes the conductivity at low Mn concentrations where isolated Mn sites act as traps for polarons moving among Cr sites. A random-barrier model describing site percolation is consistent with the measured conductivity once the Mn concentration exceeds that of the site-percolation threshold. The crossover observed in this and other mixed conducting ceramics can provide an important test of general theories which may be developed to treat hopping conduction in disordered lattices.

[1] D. P. Karim and A. T. Aldred, Phys. Rev. B **20**, 2255 (1979).

[2] W. J. Weber, C. W. Griffen, and J. L. Bates, J. Am. Ceram. Soc. **70**, 265 (1987).

[3] J. H. Kuo, H. U. Anderson, and D. M. Sparlin, J. Solid State Chem. **83**, 52 (1989); **87**, 55 (1990).

[4] S. Alexander, J. Bernasconi, W. R. Schneider, and R. Orbach, Rev. Mod. Phys. **53**, 175 (1981); J. W. Haus and K. Kehr, Phys. Rep. **150**, 265 (1987).

[5] J. W. Haus, K. Kehr, and J. W. Lyklema, Phys. Rev. B **25**, 2905 (1982); K. Kundu and P. Phillips, Phys. Rev. A **35**, 857 (1987).

[6] S. Kirkpatrick, Rev. Mod. Phys. **45**, 574 (1973).

[7] J. B. Goodenough, Phys. Rev. **164**, 785 (1967).

[8] T. Holstein, Ann. Phys. (N.Y.) **8**, 325 (1959); D. Emin and T. Holstein, Ann. Phys. (N.Y.) **53**, 439 (1969); D. Emin, Adv. Phys. **24**, 305 (1975).

[9] H. Scher and C. H. Wu, Proc. Natl. Acad. Sci. U.S.A. **78**, 22 (1980); J. Chem. Phys. **74**, 5366 (1981); V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. B **4**, 2612 (1971); P. E. Parris, Phys. Rev. B **39**, 9343 (1989).