Carrier Density Dependence of Magnetoresistance in $Tl_2Mn_{2-x}Ru_xO_7$ Pyrochlores

B. Martínez,* R. Senis, J. Fontcuberta, and X. Obradors

Institut de Ciència de Materials de Barcelona–CSIC, Campus Universitat Autònoma de Barcelona, Bellaterra 08193, Spain

W. Cheikh-Rouhou, P. Strobel, C. Bougerol-Chaillout, and M. Pernet

Laboratoire de Cristallographie–CNRS, BP 166, Grenoble Cedex 9, France

(Received 21 December 1998)

The magnetotransport properties of the $Tl_2Mn_{2-x}Ru_xO_7$ pyrochlore are studied. It is shown that Ru^{4+} substitution in the Mn^{4+} network provides a convenient way to modify the charge density in the Tl-O band without disrupting it with foreign cations. The experimental data reveal that the magnetoresistance has a quadratic dependence on the magnetization and increases when the charge density in the Tl-O conduction band is reduced. Above the Curie temperature, activated resistivity is found, signaling carrier localization and suggesting the existence of spin polarons. These results provide a solid support to recent theoretical predictions for magnetoresistance in low carrier density ferromagnets.

PACS numbers: 72.15.Gd, 75.30.Kz, 75.50.Cc

The discovery of colossal magnetoresistance (CMR) in manganese perovskites [1] has attracted much attention to these and related materials due to their potential technological applications and the extremely rich physics involved. The fundamental magnetic interaction in manganese perovskites is the double exchange (DE) mechanism [2] in which electron hopping between mixed valence Mn^{3+}/Mn^{4+} ions mediates ferromagnetic interactions leading to a ferromagnetic (FM) ordering with metallic conduction below the Curie temperature T_C. The high resistivity above T_C and the CMR is explained by the combination of both Mn^{3+}-Mn^{4+} DE and transport via Jahn-Teller polarons [3]. Suppression of the phonon-induced self-trapping of carriers when crossing T_C or under magnetic field leads to a huge reduction of resistivity.

Similar CMR response is also found in $Tl_2Mn_2O_7$ compound [4], which has a pyrochlore structure [5], but in this case neither traces of significant Mn^{3+}-Mn^{4+} mixed valence nor Jahn-Teller structural distortion [6] have been observed.

Majumdar and Littlewood (ML) have recently proposed that CMR in Mn oxides can be understood as a result of the strong scattering of a low density electron gas by spin fluctuations (SF) associated with the FM ordering of the Mn-O sublattice [7]. The necessary ingredients of this model are two separated electronic subsystems, one itinerant (weakly magnetic), and the other localized with strong magnetic interactions. These two electronic subsystems have been identified in $Tl_2Mn_2O_7$ where the itinerant charge carriers are mainly Tl 6s electrons [8], while localized moments correspond to Mn 3d electrons [4,6,9].

Up to now, efforts have been concentrated in changing the electronic transport subsystem by different substitutions on the Tl site (Sc [9], In [10], and Bi [11]). However, doping in the Tl-O sublattice necessarily disrupts the conductance of the corresponding band and thus magnetotransport properties vary in a complex manner.

In this Letter we present the first attempt concerning the modulation of the Tl-O band charge density without introducing foreign ions in the Tl-O network. For this purpose we shall take advantage of the more expanded nature of the 4d orbitals of Ru^{4+} and their tendency to form bands of metallic character—as in $SrRuO_3$ or $Tl_2Ru_2O_7$—to modify, via covalent mixing, the charge density in the Tl-O band.

The magnetotransport properties of the Tl_2Mn_{2-x}-Ru_xO_7 $(0 \leq x \leq 1)$ are here thoroughly investigated. An important change of the magnetic properties of the system, reflected in both the transition temperature T_C and the saturation magnetization M_s, is observed. Moreover, as expected, the transport properties are also strongly modified and noticeable CMR is only found for $x \leq 0.2$. In this range of compositions with noticeable CMR variable-range hopping (VRH) behavior of $\rho(T)$ curves is observed at high temperatures indicating the existence of spin polarons. These results are analyzed on the scope of the ML model [7].

The samples used in this work have been synthesized under high pressure and temperature conditions (4–6 GPa, 850–1150 °C) from the mixture of the corresponding high purity oxides. The stoichiometric mixtures were sealed in gold capsules and then a Belt-type high-pressure cell has been used for the synthesis process. The purity of the samples has been checked by using x-ray diffraction and electron microscopy [12]. The magnetic properties have been measured using a SQUID magnetometer (up to 55 kOe) and an ac susceptometer, while the four points method has been used to measure transport properties up to 80 kOe.

The magnetization vs temperature curves show quite typical ferromagnetic behavior with saturated magnetic moment very near to the expected value of $3\mu_B/Mn$ $(x = 0)$. These results are consistent with the observation of the typical λ-type peaks of the specific heat [13] and

neutron diffraction measurements [14] confirming the existence of long range FM ordering in Mn pyrochlores. Moreover, the comparison of the magnetic properties of different insulating Mn pyrochlores with that of $Tl_2Mn_2O_7$ leads to the conclusion that DE cannot explain the FM ordering observed in these materials and that superexchange is the responsible mechanism [13].

The Curie temperature T_c of the different samples, determined from the strong upturn of the real part of the ac susceptibility, $\chi'(T)$, drops rapidly as x increases, decreasing from about 140 to 80 K (see Fig. 1). The paramagnetic moment μ_{exp}, determined from $\chi'(T)$ curves in the high temperature regime ($T > 240$ K) where a Curie-Weiss behavior [$\chi' = C/(T - \theta)$] is observed, also exhibits a pronounced decrease. An effective moment μ_{eff} ($\approx 3.8 \mu_B$), corresponding to the Hund's rule for a Mn^{4+} ion, is obtained for $x = 0$. The calculated value of the magnetic moment μ_{cal} of the Tl_2Mn_{2-x}-Ru_xO_7 samples assuming a simple dilution with Ru^{4+} ions ($\mu_{eff} = 2.8\mu_B$ for low-spin state $t_2^4 e^0$ configuration) is also shown in Fig. 1. It is observed that μ_{exp} (squares) decreases much faster than μ_{cal} (solid circles). In fact, μ_{exp} behaves as if the contribution of Ru^{4+} ions to the magnetic moment were null, as indicated by the continuous line in Fig. 1. Only for $x > 1$ the Ru atoms seem to contribute to the magnetic moment [15].

The dependence of the saturation magnetization M_s, on the substitution rate x, is also shown in Fig. 1. A saturation value of M_s (50 kOe, 5 K) $\approx 2.7 \mu_B$ is obtained for the pure Mn compound ($x = 0$) in agreement with previously reported values [4,6,9,10]). As the Ru content increases, saturation magnetization decreases very fast signaling the reinforcement of antiferromagnetic (AF) interactions. The strong increase of the magnetic frustration $f = |(\theta/T_C)|$, for $x > 1.5$ also points in this direction [15]. These

observations strongly suggest that, for low Ru concentration ($x \leq 1$), Ru $4d$ electrons are no longer localized but itinerant having zero contribution to the paramagnetic moment. Therefore, it follows that a gradual modification of the conductivity upon doping should be expected.

Indeed, as shown in Fig. 2, the resistivity ρ and MR initially ($x \approx 0.05$) increase but for $x > 0.05$ slowly decrease and the former becomes very small, typical of metallic systems, at room temperature for $x = 1$ (see Fig. 2) while the latter already disappears for $x > 0.2$. Therefore, we will restrict ourselves to the range of compositions $0 \leq x \leq 0.2$ in which MR has a noticeable value.

The key observation is the strong change of resistivity detected even for very low values of x. For $T > T_C$ in the paramagnetic regime, $\rho(T)$ changes from metallic for $x = 0$ to semiconducting for higher doping. The room temperature resistivity, $\rho(300$ K) increases from 0.9 Ω cm for $x = 0$ up to almost 650 Ω cm for $x = 0.05$, while MR reaches its maximum [($\approx 95\%$ at $8T$); see Fig. 3]. This value of MR is similar to that reported previously for several authors [4,6,9,10]. Further increase of x provokes a decrease of both ρ and MR. At the same time, the low temperature metallic state progressively disappears (see Fig. 2) and the insulating-to-metal transition, characteristic of $Tl_2Ru_2O_7$, becomes apparent at $T \approx 120$ K [5,16].

For $0 \leq x \leq 0.2$ in the paramagnetic regime ($1.5T_C \leq T \leq 3T_C$) $\rho(T)$ exhibits semiconductorlike behavior with a transport mechanism that can be best described with the Mott's variable-range hopping expression (see inset of Fig. 3):

$$\rho = \rho_\infty \exp[(T_0/T)^{1/4}]. \qquad (1)$$

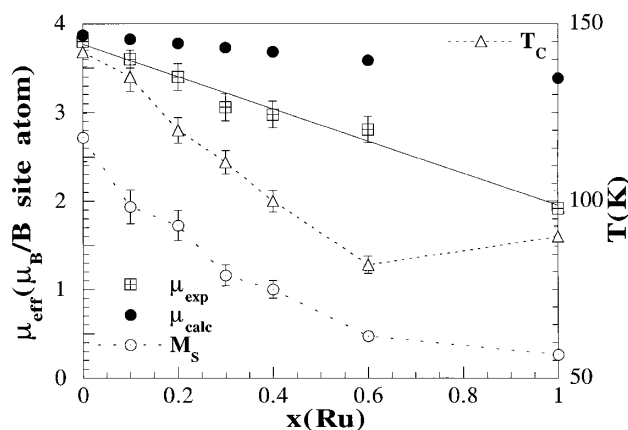The observation of a VRH-like behavior of $\rho(T)$ curves is compatible with the existence of polarons whose

FIG. 1. Variation of the paramagnetic, μ_{exp}, and the calculated, μ_{cal}, moments, transition temperature T_C and the saturation magnetization, M_s, of the $Tl_2Mn_{2-x}Ru_xO_7$ ($0 \leq x \leq 1$) compound as a function of the Ru content. The continuous line indicates the value of the magnetic moment assuming no contribution of the Ru atoms.
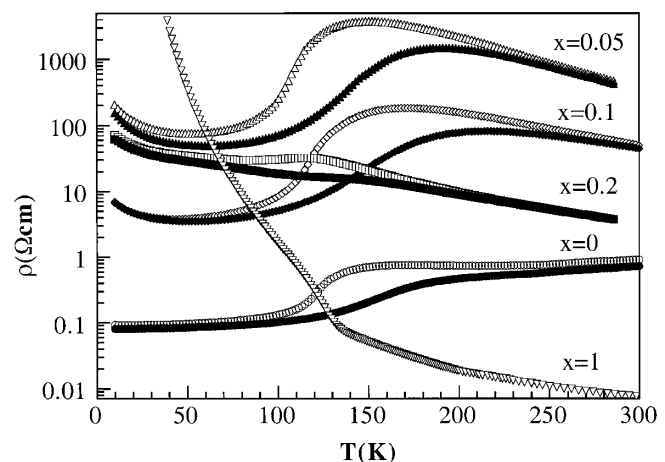

FIG. 2. Temperature dependence of the resistivity at zero field (open symbols) and 80 kOe (solid symbols) of several samples of $Tl_2Mn_{2-x}Ru_xO_7$ ($0 \leq x \leq 1$) as a function of the Ru content.
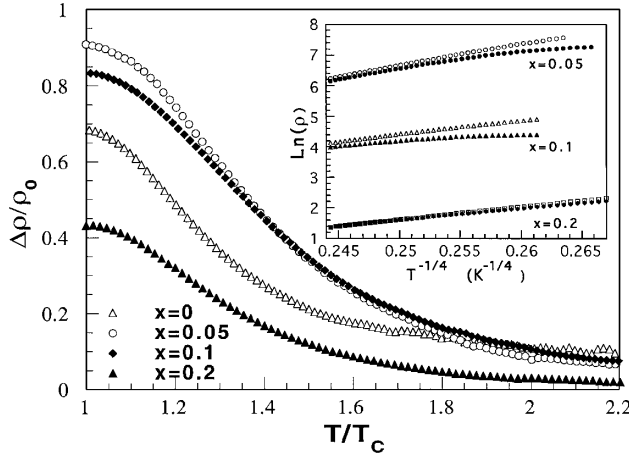
FIG. 3. Dependence of the MR on T/T_C as a function of x ($H = 60$ kOe). Inset: $\mathrm{Ln}(\rho)$ vs $T^{-1/4}$ in the paramagnetic regime for some of the samples at zero field (open symbols) and 80 kOe (solid symbols).
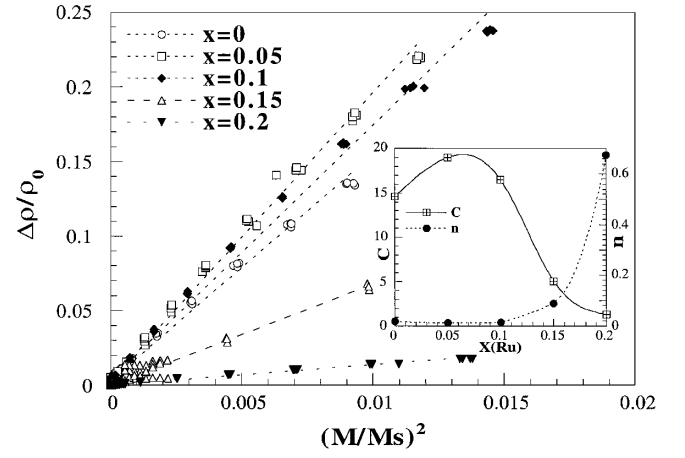

FIG. 4. Dependence of the magnetoresistance as a function of $(M/M_s)^2$ for several temperatures above T_C ($T > 1.2T_C$) and different Ru contents. Inset: Dependence of the scaling parameter C, and the density of charge carriers per magnetic unit cell $n \approx C^{-3/2}$ as a function of x.

magnetic nature is clearly evidenced in Figs. 2 and 3. Although within the ML model an activated behavior of $\rho(T)$ is expected for the conductance of spin-polarons at $T > T_C$, due to the temperature dependence of the polaron binding energy, a simple Arrhenius law $\ln\rho \sim 1/T$ should not be observed. Furthermore, it can be appreciated in Figs. 2 (solid symbols) and 3 (inset) that the $\rho(T)$ curves measured under field display a less pronounced activated behavior, which implies that the binding energy of polarons is reduced under field, thus making clear the spin nature of the polarons. The dependence on x of the T_0 $[\approx 1/N(E)]$ parameter in Eq. (1) also suggests an increase of the charge carrier density as x increases.

To allow an easier comparison with theoretical predictions, we plot in Fig. 3 the MR vs T/T_C curves for $x \leq 0.2$ samples. It can be appreciated that MR(T/T_C) displays the behavior predicted in Ref. [7] for activated transport of spin polarons.

Moreover, one of the stronger predictions of the ML model is the existence of a "scaling" between the MR and the magnetization at $T > T_C$ [7]. According to this model, at any temperature (near and above T_C) the MR should exhibit a quadratic dependence on the magnetization:

$$[\rho(0) - \rho(H)]/\rho(0) = C(M/M_s)^2, \qquad (2)$$

where M and M_s are the magnetization and saturation magnetization, respectively, and the temperature independent scaling factor, C, is related to the density of charge carriers (n) per magnetic unit cell $C \approx n^{-2/3}$.

Isothermal magnetization and field dependent resistivity curves at several temperatures above T_C indeed reveal the $(M/M_s)^2$ dependence and allow evaluation of C. In fact, it can be observed in Fig. 4 that the slope C of data taken at any temperature $T > 1.2T_C$, is temperature independent as predicted by the ML model. The different values of the scaling parameter C, as a function of x, are

shown (solid circles) in the inset of Fig. 4. Inspection of this figure reveals that for $x \approx 0$ and 0.05, the values of C are in good agreement with previous evaluations in $Tl_2Mn_2O_7$ ($C \approx 15$, [4]).

Of the highest significance is the observation that, after some initial rise of $C(x = 0.05)$, $C(x)$ decreases gradually with doping. That means that C mimics the variation of the room-temperature resistivity of the samples, i.e., the modification of the charge density upon doping. This can be more clearly seen in the inset of Fig. 4 where we also plot (squares) the variation of the charge carriers density $n \approx C^{-3/2}$ vs the Ru substitution. The increase of the charge carriers density provokes the decreases of MR since the localization mechanism is no longer effective [notice the gradual lowering of the slopes of $\rho(T)$ in Figs. 2 and 3(inset)]. MR disappears for $x > 0.2$ where $C < 2$, in agreement with the predictions of the ML model. In contrast with these results, large MR is found in manganese perovskites having $C \approx 1$–4, a fact that clearly points to the different mechanism of the MR in both materials and makes evident the relevance of the Jahn-Teller polarons in CMR in manganese perovskites [7].

Having established that both magnetic and transport measurements on Ru^{4+} substituted $Tl_2Mn_{2-x}Ru_xO_7$ ($x < 1$) pyrochlores indicate a change of the carrier density that tunes the magnetoresistance, we shall now briefly discuss the origin of this electronic transfer. It is well known that the presence of easily polarizable A type cations (such as the case of Tl^{3+}, Bi^{3+}) in Ru pyrochlores promotes metallic conductivity [17]. This behavior has been attributed to the existence of some degree of mixing of the $6s$ orbitals on the A-type cation and the Ru $4d$ orbitals [18], so that there is a net transfer of electron density from the Ru $4d$ orbitals to the Tl $6s$ orbitals. This electron transfer between the $6s$ and Ru $4d$ orbitals

is also supported by the anomalous cell size observed for metallic Ru pyrochlores [19] that can be viewed as a result of the partial oxidation of Ru. The itinerant nature of Ru $4d$ electrons has also been confirmed by our magnetic susceptibility measurements (see Fig. 1) that clearly point to a zero contribution to the paramagnetic moment. The increase of $\rho(300 \text{ K})$ for $x = 0.05$ may be simply attributed to some effect of the disorder induced in the Tl-O band by the substituting Ru ions which may decrease carrier mobility and overcome the carrier injection. As x increases, the above mentioned carrier transfer considerably increases the charge carrier density at the Tl-O band, leading to a noticeable decrease of ρ and MR that completely disappears at $x \approx 0.3$.

In summary, using the enhanced covalent bonding of Ru^{4+} ions substituting in the Mn^{4+} sublattice in the pyrochlore structure, we have shown that the conductivity, mainly associated to the Tl-O bands, can be appropriately modified. This approach, so far unexplored, may constitute a new alternative to modify the electronic properties of CMR pyrochlores. We have demonstrated that magnetoresistance in manganese pyrochlores is strongly dependent on the charge density in the conduction band, increasing largely when the itinerant charge density is depressed. This observation, together with the activated behavior of the resistivity extending up to temperatures well above T_C, signaling spin-dependent charge localization, are in agreement with recently proposed models for magnetoresistance in pyrochlores and other low-carrier density ferromagnets.

Our results strongly suggest that indeed, scattering with short-range ferromagnetic fluctuations and the formation of spin polarons are key ingredients of magnetoresistance in these systems. To this regard, although of different origin, spin polarons seem to be concomitant with the observation of CMR in manganese perovskites and pyrochlores.

---

*To whom correspondence should be addressed.

[1] R. Von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).

[2] C. Zener, Phys. Rev. **82**, 403 (1951); P. G. de Gennes, *ibid.* **118**, 141 (1960).

[3] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995); H. Röeder, J. Zhang, and A. R. Bishop, Phys. Rev. Lett. **76**, 1356 (1996).

[4] Y. Shimakawa, Y. Kubo, and T. Manako, Nature (London) **379**, 53 (1996).

[5] M. A. Subramanian, G. Aravamudan, and G. V. Subba Rao, Prog. Solid State Chem. **15**, 55 (1983).

[6] M. A. Subramanian, B. H. Toby, A. P. Ramirez, W. J. Marshall, A. W. Sleight, and G. H. Kwei, Science **273**, 81 (1996); J. W. Lynn, L. Vasiliu-Doloc, and M. A. Subramanian, Phys. Rev. Lett. **80**, 4582 (1998).

[7] P. Majundar and P. Littlewood, Phys. Rev. Lett. **81**, 1314 (1998); Nature (London) **395**, 479 (1998).

[8] D. J. Singh, Phys. Rev. B **55**, 313 (1997); D. K. Seo, M. H. Whangbo, and M. A. Subramanian, Solid State Commun. **101**, 417 (1997).

[9] A. P. Ramirez and M. A. Subramanian, Science **277**, 546 (1997).

[10] S. W. Cheong, H. Y. Wang, B. Batlogg, and L. W. Rupp, Jr., Solid State Commun. **98**, 163 (1996).

[11] J. A. Alonso, J. L. Martínez, M. J. Martínez-Lope, M. T. Casais, and M. T. Fernández-Díaz, Phys. Rev. Lett. **82**, 189 (1999).

[12] W. Cheihk-Rouhou, P. Strobel, C. Bougerol-Chaillout, S. M. Loureiro, R. Senis, B. Martinez, X. Obradors, and J. Pierre, J. Mater. Chem. **9**, 743 (1999).

[13] Y. Shimakawa, Y. Kubo, N. Hamada, J. D. Jorgensen, Z. Hu, S. Short, M. Nohara, and H. Takagi, Phys. Rev. B **59**, 1249 (1999).

[14] Y. Shimakawa, Y. Kubo, T. Manako, Y. V. Sushko, D. N. Argyriou, and J. D. Jorgensen, Phys. Rev. B **55**, 6399 (1997).

[15] R. Senis, B. Martinez, J. Fontcuberta, W. Cheikh-Rouhou, P. Strobel, C. Bougerol-Chaillout, and M. Pernet (to be published).

[16] R. Senis, B. Martinez, J. Fontcuberta, X. Obradors, W. Cheikh-Rouhou, P. Strobel, C. Bougerol-Chaillout, and M. Pernet, J. Appl. Phys. (to be published).

[17] P. A. Cox, J. B. Goodenough, P. J. Taverner, D. Telles, and R. G. Egdell, J. Solid State Chem. **62**, 360 (1986).

[18] W. Y. Shu, R. V. Kasowski, T. Miller, and Tai-Chang Chiang, Appl. Phys. Lett. **52**, 792 (1988).

[19] B. J. Kennedy, Physica (Amsterdam) **241B–243B**, 303 (1998).