

# Unprecedented magnetoresistance in Cd-substituted $Tl_2Mn_2O_7$ pyrochlores

J. A. Alonso,<sup>a)</sup> P. Velasco, M. J. Martínez-Lope, M. T. Casais, and J. L. Martínez  
*Instituto de Ciencia de Materiales de Madrid, C.S.I.C., Cantoblanco, E-28049 Madrid, Spain*

María T. Fernández-Díaz  
*Institut Laue-Langevin, B.P. 156, F-38042 Grenoble Cedex 9, France*

J. M. de Paoli  
*Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, 5000 Córdoba, Argentina*

(Received 7 January 2000; accepted for publication 3 April 2000)

Moderate pressure techniques ( $P=20$  kbar) have been used to prepare  $Tl_{2-x}Cd_xMn_2O_7$  ( $0 \leq x \leq 0.4$ ) pyrochlore-like materials. The  $x=0.2$  compound has been characterized by neutron powder diffraction, magnetic, magnetotransport, and Hall measurements. This material is ferromagnetic below  $T_C=110$  K. Both electrical resistance and magnetoresistance (MR) are enhanced with respect to stoichiometric  $Tl_2Mn_2O_7$ , due to the drastic reduction in the number of carriers (electrons) induced by hole doping. MR(0.5 T) is higher than 10<sup>6</sup>% at 120 K, and MR(9 T) is 30% at room temperature. We show that hole doped derivatives of  $Tl_2Mn_2O_7$  are promising candidates in which to search for large bulk magnetoresistance. © 2000 American Institute of Physics.  
 [S0003-6951(00)00822-6]

Half metallic ferromagnets have attracted much attention as a source of magnetoresistive materials, the electrical conductivity of which changes upon application of an external magnetic field.<sup>1</sup> Widespread interest in the scientific community was sparked when large values of magnetoresistance (MR) were described at first for hole-doped manganese perovskites,  $R_{1-x}A_xMnO_3$  ( $R$ =rare-earths;  $A$ =alkali-earths),<sup>2,3</sup> and then for other ferromagnets such as the double perovskites  $A_2FeMoO_6$ ,<sup>4</sup> or the pyrochlore  $Tl_2Mn_2O_7$ .<sup>5-7</sup> Among them, Tl-containing pyrochlores have been less studied since they can only be prepared under high pressures. In contrast with manganese perovskites, in  $Tl_2Mn_2O_7$  there is no  $Mn^{3+}-Mn^{4+}$  mixed valence or Jahn-Teller distortions in the  $MnO_6$  octahedra;<sup>7</sup> the ferromagnetism ( $T_C=120$  K)<sup>8</sup> is a consequence of superexchange<sup>8,9</sup> interactions between  $Mn^{4+}$  magnetic moments and the metallic conductivity results from the partial filling of the Tl  $6s$  block bands, through the overlapping between Mn  $t_{2g}$ , O  $2p$ , and Tl  $6s$  bands.<sup>10,11</sup>

Majumdar and Littlewood<sup>12</sup> showed that MR in a wide variety of ferromagnetic (FM) semimetals scales with the number of charge carriers, as  $\Delta\rho/\rho_0 \approx n^{-2/3}(M/M_s)^2$ , where  $n$  is the carriers density per magnetic unit cell, and  $M$  and  $M_s$  stand for the magnetization and saturation magnetization, respectively. This is a result of the scattering of a low-density electron gas by spin fluctuations concomitant with the FM long range ordering or local spin bags of the magnetic cations. According to this model, the MR can be tuned by properly modifying the carrier density of a given material. Enhanced MR properties should be found in ferromagnetic insulators suitably converted into semimetals by chemical doping, thus injecting a conveniently small number of carriers.

Recently, some efforts have been devoted to tuning and optimizing the MR properties of  $Tl_2Mn_2O_7$  related pyro-

chlores by substitution in both Tl and Mn sublattices. Tl atoms have been replaced by In,<sup>13</sup> Sc,<sup>14</sup> and Bi,<sup>15</sup> leading to different modifications of the physical properties. Perhaps the most dramatic changes have been described for the  $Tl_{2-x}Bi_xMn_2O_7$  ( $0 \leq x \leq 0.5$ ) pyrochlore series,<sup>15</sup> in which magnetoresistance increases up to 10<sup>5</sup>% with Bi substitution. The Mn atoms have also been partially replaced by Ru<sup>16,17</sup> and Sb.<sup>18</sup> In particular, moderate Sb substitution leads to a significant increment of  $T_C$ , up to 200 K for  $x=0.2$ ,<sup>18</sup> however the MR factors are lower than for the pure compound.

In this letter we describe the preparation of a novel series, obtained by substituting Cd for Tl in  $(Tl_{2-x}Cd_x)Mn_2O_7$  in a relatively wide compositional range,  $0 \leq x \leq 0.4$ . We report the results of an in-depth study of the  $x=0.2$  compound, including structural neutron powder diffraction (NPD) data. Materials with nominal  $x=0, 0.1, 0.2, 0.4$  were prepared under high pressure conditions, from stoichiometric mixtures of  $Tl_2O_3$ , CdO, and  $MnO_2$ , heated at 1000 °C for 1 h at 20 kbar. The reaction products were characterized by x-ray diffraction with Cu  $K\alpha$  radiation. Single-phase cubic pyrochlores were identified, as illustrated in Fig. 1, for the  $x$

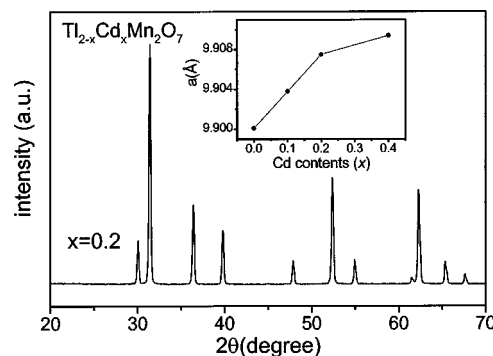


FIG. 1. XRD pattern for  $Tl_{1.8}Cd_{0.2}Mn_2O_7$ , cubic with  $a=9.9075(1)$  Å. The inset shows the unit cell parameters variation for the series  $Tl_{2-x}Cd_xMn_2O_7$  ( $x=0,0.1,0.2,0.4$ ).

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: ja.alonso@icmm.csic.es

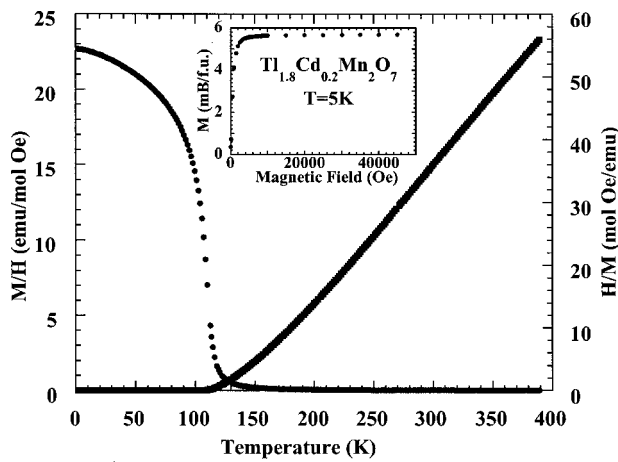


FIG. 2. dc susceptibility as a function of temperature for  $\text{Tl}_{1.8}\text{Cd}_{0.2}\text{Mn}_2\text{O}_7$ . The inset shows the magnetization vs magnetic field at 5 K.

$=0.2$  compound. The inset of Fig. 1 shows that the lattice parameter monotonically increases with  $x$ , from  $a = 9.9004(1) \text{ \AA}$  for  $\text{Tl}_2\text{Mn}_2\text{O}_7$ , to  $a = 9.9094(1) \text{ \AA}$  for  $\text{Tl}_{1.6}\text{Cd}_{0.4}\text{Mn}_2\text{O}_7$ . This variation is consistent with the larger ionic radius<sup>19</sup> for  $\text{Cd}^{2+}$  ( $1.10 \text{ \AA}$ ) compared with that for  $\text{Tl}^{3+}$  ( $0.98 \text{ \AA}$ ), in eightfold coordination.  $\text{Cd}^{2+}$  cations are well known to occupy A positions in many pyrochlore-like compounds.<sup>20</sup> From the chemical point of view, the presence of  $x \text{ Cd}^{2+}$  cations in the  $\text{Tl}^{3+}$  sublattice of  $\text{Tl}_{2-x}\text{Cd}_x\text{Mn}_2\text{O}_7$  implies either the oxidation of  $x \text{ Mn}^{4+}$  to  $\text{Mn}^{5+}$  cations or the presence of  $x/2$  oxygen vacancies per formula unit. A NPD study was useful to decide between both possibilities and investigate the structural details of the Cd-substituted samples. A room temperature high resolution NPD pattern of  $\text{Tl}_{1.8}\text{Cd}_{0.2}\text{Mn}_2\text{O}_7$  was collected at the D2B diffractometer of the Institut Laue-Langevin, Grenoble, with a wavelength  $\lambda = 1.594 \text{ \AA}$ . The sample, weighing 0.8 g, was packed in a double-walled vanadium holder, to minimize the Cd absorption.

The refinement of the NPD pattern for the  $x=0.2$  material was performed by the Rietveld method in a conventional pyrochlore structural model, space group  $Fd-3m$ ,  $a = 9.9075(1) \text{ \AA}$ ,  $Z=8$ , considering Tl and Cd atoms distributed at random at  $16c$   $(0,0,0)$  positions, Mn at  $16d$   $(1/2, 1/2, 1/2)$  sites, O at  $48f$   $(u, 1/8, 1/8)$ ,  $u = 0.4258(1)$ , and  $\text{O}'$  at  $8a$   $(1/8, 1/8, 1/8)$  positions, reaching the agreement factors  $R_p = 2.10\%$ ,  $R_{wp} = 2.68\%$ ,  $\chi^2 = 2.35$ , and  $R_I = 7.01\%$ . The final crystallographic composition is  $[\text{Tl}_{1.73(2)}\text{Cd}_{0.27(2)}]_c \text{ sites} [\text{Mn}_2]_d \text{ sites} \text{O}_{7.01(1)}$ . There is no measurable deficiency at  $\text{O}'$  positions. We conclude that the incorporation of  $\text{Cd}^{2+}$  to the A positions probably involves the occurrence of some mixed  $\text{Mn}^{4+}-\text{Mn}^{5+}$  valence at the B sublattice. The Mn–O distance observed for  $\text{Tl}_{1.8}\text{Cd}_{0.2}\text{Mn}_2\text{O}_7$ , of  $1.8983(8) \text{ \AA}$ , is significantly shorter than that observed for the nonsubstituted pyrochlore of  $1.9034(4) \text{ \AA}$ , in spite of the expansion observed in the unit-cell volume. This is due to the significant change of the  $u$  parameter ( $u = 0.4247(1)$  in the undoped compound), and it is consistent with the incorporation of smaller  $\text{Mn}^{5+}$  cations in the  $\text{Mn}^{4+}$  sublattice.

The dc magnetic susceptibility versus temperature data for  $\text{Tl}_{1.8}\text{Cd}_{0.2}\text{Mn}_2\text{O}_7$  (Fig. 2), measured with a commercial superconducting quantum interference device magnetometer,

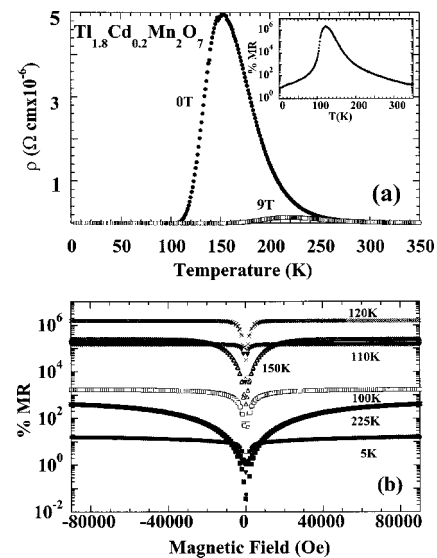


FIG. 3. (a) Resistivity vs temperature plots at  $H=0$  and 9 T, for  $\text{Tl}_{1.8}\text{Cd}_{0.2}\text{Mn}_2\text{O}_7$ ; the inset shows the temperature variation of  $\text{MR}(9 \text{ T})$ . (b) MR vs field isotherms.  $\text{MR}(H) = 100 \times (R(0) - R(H)) / R(H)$ .

exhibit the low temperature saturation characteristic of a spontaneous ferromagnetic ordering, with  $T_C = 110 \text{ K}$ . The magnetization versus magnetic field data at 5 K represented in the inset show that a complete saturation of the magnetic moments,  $M = 5.7 \mu_B/\text{formula}$ , is reached. The inverse susceptibility  $1/\chi$  follows a Curie–Weiss behavior only for temperatures  $T > 300 \text{ K}$ , well above  $T_C$ , suggesting the presence of a polaronic medium. A paramagnetic moment ( $p$ ) of  $5.42 \mu_B$  per formula unit (expected is  $5.47 \mu_B$  for spin-only  $\text{Mn}^{4+}$ ) is observed from the Curie–Weiss fit.

The transport and magnetotransport properties of  $\text{Tl}_{1.8}\text{Cd}_{0.2}\text{Mn}_2\text{O}_7$  are shown in Fig. 3. There is a dramatic change in the overall behavior of the resistivity curve with respect to the  $x=0$  compound.<sup>7</sup> An abrupt increase in the  $\rho(H=0)$  is observed as the temperature decreases, reaching a maximum at  $T = 153 \text{ K}$ . This is consistent with the smaller number of charge carriers found for this compound from Hall measurements: given in electrons per unit cell,  $n = 0.005$  for  $x=0$ ,<sup>11</sup> and  $n = 0.0002$  for  $x=0.2$ . However, the most dramatic feature is the magnetoresistive behavior: the resistance under a magnetic field of 9 T decreases by 6 orders of magnitude at 120 K. The magnetoresistance, defined as  $\text{MR}(H) = 100 \times (R(0) - R(H)) / R(H)$ , reaches values higher than  $2 \times 10^6\%$  at 120 K, as shown in the inset and in Fig. 3(b). Note that at 120 K MR is saturated for fields higher than 1 T; at low fields such as  $H = 0.5 \text{ T}$  the MR is still higher than  $10^6\%$ . This is greatly superior to the results found for  $\text{Tl}_{1.8}\text{Sc}_{0.2}\text{Mn}_2\text{O}_7$ , showing a MR (6 T) of  $5.8 \times 10^3\%$  at  $T = 125 \text{ K}$ ,<sup>14</sup> and for  $\text{Tl}_{1.8}\text{Bi}_{0.2}\text{Mn}_2\text{O}_7$ , yielding  $\text{MR}(9 \text{ T}) = 10^4\%$  at 110 K and  $10^5\%$  at 10 K.<sup>15</sup> This is related to the considerable contribution of the spin fluctuation scattering to  $\rho$  near  $T_C$ , which are suppressed when the external field is applied. The room-temperature behavior is also remarkable for  $\text{Tl}_{1.8}\text{Cd}_{0.2}\text{Mn}_2\text{O}_7$ : the inset of Fig. 3(a) shows a  $\text{MR}(9 \text{ T})$  value of 30% at 300 K. The present results demonstrate that Cd substitution may enhance MR up to levels which make it possible to propose pyrochlore-like materials as candidates for technical applications.

The observed increase in MR is concomitant with a de-

crease in the number of charge carriers from  $x=0$  to  $x=0.2$  compounds, according to the model by Majumdar and Littlewood.<sup>12</sup> One would be tempted to attribute the increase in resistance at zero field to the disorder induced in the Tl–O bands through Cd<sup>2+</sup> substitution. Probably, this effect is only partially responsible for this phenomenon: other substitutions in the Tl sublattice previously reported (In<sup>3+</sup>,<sup>13</sup> Sc<sup>3+</sup>,<sup>14</sup> and Bi<sup>3+</sup>)<sup>15</sup> lead to smaller increments in MR, for the same percentages of replacement (10%) and disorder. The key factor for the dramatic decrease in the number of charge carriers is the introduction of a divalent element into the Tl<sup>3+</sup> sublattice. As demonstrated from electronic band structure calculation for undoped Tl<sub>2</sub>Mn<sub>2</sub>O<sub>7</sub>,<sup>10,11</sup> one of the down-spin bands, which is strongly hybridized among Tl(6*s*), O(2*p*), and Mn(3*d*), crosses the Fermi energy and overlaps with the up-spin valence band. The number of electrons in the Fermi surface is about 0.005 per unit cell. The replacement of Tl<sup>3+</sup> for Cd<sup>2+</sup> introduces holes in the structure, probably localized at Mn positions: the observed shortening of the Mn–O distances suggests an increase in the oxidation state of Mn. These holes are not mobile, since they are located at the Mn–O sublattice, and do not contribute to the electronic transport. But, at the same time, the presence of Cd<sup>2+</sup> hinders the electronic transfer from (Tl, Cd) sublattice to the mentioned down-spin bands, substantially decreasing the number of electrons at the Fermi surface. In other words, the effect of Cd doping is the impoverishment in electrons of the (Tl, Cd) sublattice, thus impairing the electron filling of the Tl–Mn–O bands.

We have shown that moderate pressure synthesis techniques can be used to prepare a Cd-substituted series of pyrochlores based on Tl<sub>2</sub>Mn<sub>2</sub>O<sub>7</sub>, in which MR is hugely enhanced. We propose an effective way of increasing resistance and MR in thallium pyrochlores by doping the Tl<sup>3+</sup> sublattice with divalent cations, which substantially decreases the number of mobile carriers (electrons) by hinder-

ing the electronic transfer towards the down-spin Tl–Mn–O bands responsible for the electronic transport.

The authors are grateful for the financial support of CICYT (Project Nos. PB97-1181 and MAT99-1045) and to ILL for making all facilities available.

- <sup>1</sup>A. P. Ramirez, *J. Phys.: Condens. Matter* **9**, 8171 (1997).
- <sup>2</sup>R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, *Phys. Rev. Lett.* **71**, 2331 (1993).
- <sup>3</sup>S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, *Science* **246**, 413 (1994).
- <sup>4</sup>K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, *Nature (London)* **395**, 677 (1998).
- <sup>5</sup>Y. Shimikawa, Y. Kubo, and T. Manako, *Nature (London)* **379**, 53 (1996).
- <sup>6</sup>M. A. Subramanian, B. H. Toby, A. P. Ramirez, W. J. Marshall, A. W. Sleight, and G. H. Kwei, *Science* **273**, 81 (1996).
- <sup>7</sup>Y. Shimikawa, Y. Kubo, T. Manako, Y. V. Sushko, D. N. Argyriou, and J. D. Jorgensen, *Phys. Rev. B* **55**, 6399 (1997).
- <sup>8</sup>J. H. Zhao, H. P. Kunkel, X. Z. Zhou, G. Williams, and M. A. Subramanian, *Phys. Rev. Lett.* **83**, 219 (1999).
- <sup>9</sup>E. Granado, P. G. Pagliuso, J. A. Sanjurjo, C. Rettori, M. A. Subramanian, S.-W. Cheong, and S. B. Oseroff, *Phys. Rev. B* **60**, 6513 (1999).
- <sup>10</sup>D. J. Singh, *Phys. Rev. B* **55**, 313 (1997).
- <sup>11</sup>Y. Shimakawa, Y. Kubo, N. Hamada, J. D. Jorgensen, Z. Zu, S. Short, N. Nohara, and H. Takagi, *Phys. Rev. B* **59**, 1249 (1999).
- <sup>12</sup>P. Majumdar and P. B. Littlewood, *Nature (London)* **395**, 479 (1998).
- <sup>13</sup>S.-W. Cheong, H. Y. Hwang, B. Batlogg, and L. W. Rupp, *Solid State Commun.* **98**, 163 (1996).
- <sup>14</sup>A. P. Ramirez and M. A. Subramanian, *Science* **277**, 546 (1997).
- <sup>15</sup>J. A. Alonso, J. L. Martínez, M. J. Martínez-Lope, M. T. Casais, and M. T. Fernández-Díaz, *Phys. Rev. Lett.* **82**, 189 (1999).
- <sup>16</sup>W. Cheikh-Rouhou, P. Strobel, C. Chaillout, S. M. Loureiro, R. Senis, B. Martínez, X. Obradors, and J. Pierre, *J. Mater. Chem.* **9**, 743 (1999).
- <sup>17</sup>B. Martínez, R. Senis, J. Fontcuberta, X. Obradors, W. Cheikh-Rouhou, P. Strobel, C. Bourgerol-Chaillout, and P. Pernet, *Phys. Rev. Lett.* **83**, 2022 (1999).
- <sup>18</sup>J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, P. Velasco, J. L. Martínez, M. T. Fernández-Díaz, and J. M. de Paoli, *Phys. Rev. B* **60**, R15024 (1999).
- <sup>19</sup>R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys. Diff., Theor. Gen. Crystallogr.* **32**, 751 (1976).
- <sup>20</sup>M. A. Subramanian, G. Aravamudan, and G. V. Subba Rao, *Prog. Solid State Chem.* **15**, 55 (1983).