Unprecedented magnetoresistance in Cd-substituted Tl$_2$Mn$_2$O$_7$ pyrochlores

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Moderate pressure techniques ($P=20$ kbar) have been used to prepare Tl$_{2-x}$Cd$_x$Mn$_2$O$_7$ ($0 \leq x \leq 0.4$) 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$_2$Mn$_2$O$_7$, due to the drastic reduction in the number of carriers (electrons) induced by hole doping. MR(0.5 T) is higher than 10$^6$% at 120 K, and MR(9 T) is 30% at room temperature. We show that hole doped derivatives of Tl$_2$Mn$_2$O$_7$ are promising candidates in which to search for large bulk magnetoresistance. © 2000 American Institute of Physics.

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. Widespread interest in the scientific community was sparked when large values of magnetoresistance were described at first for hole-doped manganese perovskites, R$_1$-$A$MnO$_3$ (R=rare-earths; A=alkali-earths), and then for other ferromagnets such as the double perovskites $A_2$FeMoO$_6$ or the pyrochlore Tl$_2$Mn$_2$O$_7$. 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$_2$Mn$_2$O$_7$ there is no Mn$^{3+}$–Mn$^{4+}$ mixed valence or Jahn–Teller distortions in the MnO$_6$ octahedra; the ferromagnetism ($T_C=120$ K) is a consequence of superexchange interactions between Mn$^{4+}$ magnetic moments and the metallic conductivity results from long range ordering or local spin bags of the magnetic crystal. Therefore, we show that hole doped derivatives of Tl$_2$Mn$_2$O$_7$ are promising candidates in which to search for large bulk magnetoresistance.

In this letter we describe the preparation of a novel series, obtained by substituting Cd for Tl in (Tl$_{2-x}$Cd$_x$)Mn$_2$O$_7$ 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$_2$O$_3$, Cd$_2$O$_3$, and Mn$_2$O$_3$, heated at 1000°C for 1 h at 20 kbar. The reaction products were characterized by x-ray diffraction with Cu Kα radiation. Single-phase cubic pyrochlores were identified, as illustrated in Fig. 1, for the $x$

![FIG. 1. XRD pattern for Tl$_{2-x}$Cd$_x$Mn$_2$O$_7$, cubic with $a=9.9075(1)$ Å. The inset shows the unit cell parameters variation for the series Tl$_{2-x}$Cd$_x$Mn$_2$O$_7$ ($x=0.0,0.1,0.2,0.4$).]
For $Tl_{1.8}Cd_{0.2}Mn_2O_7$ compound. The inset of Fig. 1 shows that the lattice parameter monotonically increases with $x$, from $a = 9.9004(1)$ Å for $Tl_2Mn_2O_7$, to $a = 9.9094(1)$ Å for $Tl_{1.8}Cd_{0.2}Mn_2O_7$. This variation is consistent with the larger ionic radius for Cd$^{2+}$ (1.10 Å) compared with that for Tl$^{3+}$ (0.98 Å), in eightfold coordination. Cd$^{2+}$ cations are well known to occupy A positions in many pyrochlore-like compounds. From the chemical point of view, the presence of $x$ Cd$^{2+}$ cations in the Tl$^{3+}$ sublattice of $Tl_{1.8}Mn_2O_7$ implies either the oxidation of $x$ Mn$^{4+}$ to 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 $Tl_{1.8}Cd_{0.2}Mn_2O_7$ was collected at the D2B diffractometer of the Institut Laue-Langevin, Grenoble, with a wavelength $\lambda = 1.594$ Å. 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 $Fd\overline{3}m$, $a = 9.9075(1)$ Å, $Z = 8$, considering Tl and Cd atoms distributed at random at 16$c$ (0,0,0) positions, Mn at 16$d$ (1/2, 1/2, 1/2) sites, O at 48$f$ (u, 1/8, 1/8), $u = 0.4258(1)$, and O$^\prime$ at 8$a$ (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 $[Tl_{1.73(2)}Cd_{0.27(2)}]_{c\text{sites}}(Mn_{2.3}\text{d sites}O_{7.01(1)})$. There is no measurable deficiency at O$^\prime$ positions. We conclude that the incorporation of Cd$^{2+}$ to the A positions probably involves the occurrence of some mixed Mn$^{4+}$–Mn$^{5+}$ valence at the B sublattice. The Mn–O distance observed for $Tl_{1.8}Cd_{0.2}Mn_2O_7$, of 1.8983(8) Å, is significantly shorter than that observed for the nonsubstituted pyrochlore of 1.9034(4) Å, 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 Mn$^{5+}$ cations in the Mn$^{4+}$ sublattice.

The dc magnetic susceptibility versus temperature data for $Tl_{1.8}Cd_{0.2}Mn_2O_7$ (Fig. 2), measured with a commercial superconducting quantum interference device magnetometer, exhibit the low temperature saturation characteristic of a spontaneous ferromagnetic ordering, with $T_C = 110$ K. The magnetization versus magnetic field at 5 K represented in the inset show that a complete saturation of the magnetic moments, $M = 5.7\,\mu_B$/formula, is reached. The inverse susceptibility $1/\chi$ follows a Curie–Weiss behavior only for temperatures $T > 300$ K, well above $T_C$, suggesting the presence of a polaronic medium. A paramagnetic moment ($\rho$) of 5.42 $\mu_B$ per formula unit (expected is 5.47 $\mu_B$ for spin-only Mn$^{4+}$) is observed from the Curie–Weiss fit.

The transport and magnetotransport properties of $Tl_{1.8}Cd_{0.2}Mn_2O_7$ 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. An abrupt increase in the $\rho(H = 0)$ is observed as the temperature decreases, reaching a maximum at $T = 153$ 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 $x = 0$ 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 $MR(H) = 100\times(R(0) - R(H))/R(0)$, reaches values higher than $2\times10^4\%$ 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 $H = 0.5$ T the MR is still higher than $10^6\%$. This is greatly superior to the results found for $Tl_{1.8}Sc_{0.2}Mn_2O_7$, showing a MR (6 T) of $5.8 \times 10^3\%$ at $T = 125$ K. For $Tl_{1.8}Bi_{0.2}Mn_2O_7$, yielding $MR(9\,T) = 10^5\%$ at 110 K and $10^6\%$ at 10 K, 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 $Tl_{1.8}Cd_{0.2}Mn_2O_7$: the inset of Fig. 3(a) shows a MR(9 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 decrease of the magnetic susceptibility. The inset of Fig. 3 shows the temperature variation of $MR(9\,T)$, with $T_C = 110$ K. The magnetization versus magnetic field at 5 K exhibited the low temperature saturation characteristic of a spontaneous ferromagnetic ordering, showing a complete saturation of the magnetic moments, $M = 5.7\,\mu_B$/formula. The inverse susceptibility $1/\chi$ follows a Curie–Weiss behavior only for temperatures $T > 300$ K, well above $T_C$, suggesting the presence of a polaronic medium. A paramagnetic moment ($\rho$) of 5.42 $\mu_B$ per formula unit (expected is 5.47 $\mu_B$ for spin-only Mn$^{4+}$) is observed from the Curie–Weiss fit.
crease in the number of charge carriers from \(x = 0\) to \(x = 0.2\) compounds, according to the model by Majumdar and Littlewood.\(^{12}\) One would be tempted to attribute the increase in resistance at zero field to the disorder induced in the Tl–O bands through Cd\(^{2+}\) substitution. Probably, this effect is only partially responsible for this phenomenon: other substitutions in the Tl sublattice previously reported (In\(^{3+}\), Sc\(^{3+}\), and Bi\(^{3+}\))\(^{15}\) 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\(^{3+}\) sublattice. As demonstrated from electronic band structure calculation for undoped Tl\(_2\)Mn\(_2\)O\(_7\),\(^{10,11}\) one of the down-spin bands, which is strongly hybridized among Tl\((6s, O(2p))\), and Mn\((3d)\), 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\(^{3+}\) for Cd\(^{2+}\) 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\(^{2+}\) 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\(_2\)Mn\(_2\)O\(_7\), in which MR is hugely enhanced. We propose an effective way of increasing resistance and MR in thallium pyrochlores by doping the Tl\(^{3+}\) sublattice with divalent cations, which substantially decreases the number of mobile carriers (electrons) by hindering the electronic transfer towards the down-spin Tl–Mn–O bands responsible for the electronic transport.

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