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First-order transition and phase separation in pyrochlores with colossal magnetoresistance

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$Tl_2Mn_2O_7$ pyrochlores present colossal magnetoresistance (CMR) around the long-range ferromagnetic ordering temperature (T_C). The character of this magnetic phase transition has been determined to be first order, by purely magnetic methods, in contrast to the second order character previously reported by Zhao *et al.* [Phys. Rev. Lett. **83**, 219 (1999)]. The highest CMR effect, as in $Tl_{1.8}Cd_{0.2}Mn_2O_7$, corresponds to a stronger first order character. This character implies a second type of magnetic interaction, in addition to the direct superexchange between the Mn^{4+} ions, as well as a phase coexistence. A model is proposed, with a complete Hamiltonian (including superexchange and an indirect interaction), which reproduce the observed phenomenology.

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Very large values of colossal magnetoresistance (CMR) have been described for $Tl_2Mn_2O_7$-related pyrochlores, around the ferromagnetic ordering temperature (T_C). The $Tl_2Mn_2O_7$ compound (undoped system) contains only Mn^{4+}. Therefore CMR is not related to the Jahn-Teller effect nor to the double exchange mechanism, associated with the mixed valence Mn^{3+}-Mn^{4+} in manganese perovskites. Initial data analysis[1–4] attributed the long-range ferromagnetic ordering to a direct superexchange interaction Mn^{4+}-O-Mn^{4+}. Later on, the critical exponents were measured by Zhao *et al.*[5] indicating a second order character of the magnetic transition. These exponent values were very close to those predicted for a near-neighbor (NN) Heisenberg three-dimensional (3D) system. Hence, the system was considered as a well known NN Heisenberg system and a simple and coherent picture was established. Subsequently, the decrease of T_C on hydrostatic pressure data[6] in $Tl_2Mn_2O_7$, as well as the big difference in T_C between the isomorphous systems $Tl_2Mn_2O_7$, $In_2Mn_2O_7$, $Lu_2Mn_2O_7$, and $Y_2Mn_2O_7$, $T_C \simeq 130$, 129, 15, and 16 K, respectively,[7] pointed out to a more complex system than assumed until then. Recently, Nuñez-Regueiro and Lacroix[8] made a careful calculation, using a perturbation expansion in the Mn-O hopping term, which reproduces either the difference in T_C, depending on the different ions (Tl, In, Lu, and Y), as well as the low pressure dependence of T_C. In order to explain the increase of T_C at much higher hydrostatic pressure,[8,9] a new indirect interaction between the Mn (t_{2g}) localized band mediated by the Tl($6s$)-O($2p$)-Mn(e_g) correlated bands is taken into account.

There were several reports on the $Tl_2Mn_2O_7$ family that, from the theoretical point of view, proposed to explain the long-range ferromagnetic ordering as a more complex system.[4,8,10–12] In that sense the character of the magnetic transition is a very important issue because only a simple NN Heisenberg 3D system is compatible with a second order character of the magnetic phase transition. The purpose of the present letter is mostly to study in detail the character of the long range ferromagnetic transition, in different samples of the $Tl_2Mn_2O_7$ family, with different ordering temperatures and CMR effects, as a fundamental issue to understand the magnetic interactions in this system.

Polycrystalline samples of $Tl_2Mn_2O_7$, $Tl_{1.8}Cd_{0.2}Mn_2O_7$, and $Tl_2Mn_{1.8}Sb_{0.2}O_7$ pyrochlores were prepared under high pressure conditions, from stoichiometric amounts of the corresponding oxides Tl_2O_3, MnO_2, CdO, Sb_2O_3. All the details of the sample preparation and structural characterization (x-ray and neutron diffraction) are given elsewhere.[13–15] The magnetic susceptibility was measured with a commercial superconducting quantum interference device (SQUID) magnetometer, in the range from 2 to 300 K and magnetic fields up to 5 T. Transport and magnetotransport measurements were performed by the four-point contact technique inside a physical properties measurement system (PPMS) cryostat from Quantum Design (San Diego, USA) in the range from 2 to 350 K and magnetic fields up to 9 T. The specific heat was measured inside the same cryostat using a quasiadiabatic heat pulse relaxation method. The thermopower measurements were done using a standard constant ΔT method, in a temperature range from 5 to 400 K.

The possibility of considering the magnetic phase transition as a first-order one was first explored theoretically by Bean and Rodbell.[16] For that purpose they considered a compressible material with an exchange interaction strongly dependent upon the interatomic spacing. They found that in such case, for an hypothetical second-order transition, the expansion of the Gibbs free energy in terms of magnetization should have, at the Curie temperature, a null quadratic term and a positive quartic one. Banerjee[17] detected the essential similarity between this result and the Landau-Lifshitz criterion[18] and condensed them into one that provides a tool to distinguish first-order magnetic transitions from second-order ones. It consists on the analysis of the sign of the quartic term of the Gibbs free energy,[17] which is quite simple to obtain graphically, simply observing the slope of isotherm plots of H/M vs M^2. A positive or negative slope indicates the second- or first-order character of the transition, respectively. It is worth mentioning that this procedure allows the identification of the character of the transition by purely magnetic methods, in a very effective way, as sucessfully proved by Mira *et al.* in $La_{2/3}(Ca,Sr)_{1/3}MnO_3$ perovskites.[19,20]

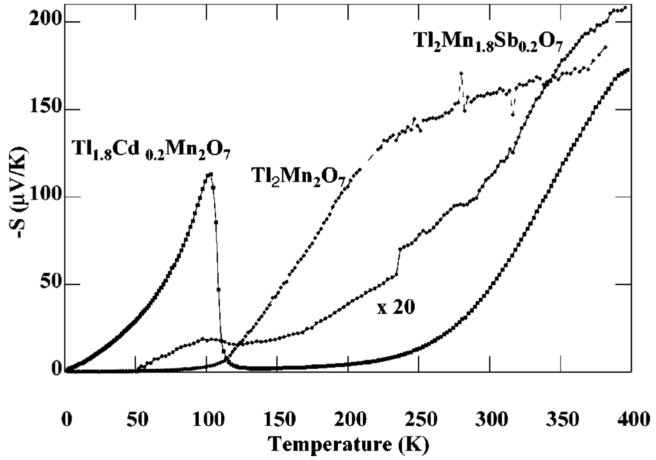

FIG. 1. Temperature dependence of the thermopower for $Tl_2Mn_2O_7$, $Tl_{1.8}Cd_{0.2}Mn_2O_7$, and $Tl_2Mn_{1.8}Sb_{0.2}O_7$, these later data are 20 times smaller. Strong variation of S is observed around T_C. The lines are a guide to the eye.

The dc-magnetization measurements, performed at 100 Oe, show a T_C of 130 K for the undoped material, whereas Cd doping decreases T_C ($\simeq 110$ K), and Sb doping increases it ($T_C \simeq 190$ K). As already reported[13–15] the resistivity changes strongly between the three compounds with values at 300 K of 20 Ω cm, 0.2 Ω cm, and 30 kΩ cm for $Tl_2Mn_2O_7$, $Tl_2Mn_{1.8}Sb_{0.2}O_7$, and $Tl_{1.8}Cd_{0.2}Mn_2O_7$, respectively. In all cases the ferromagnetic ordering is accompanied by a sudden drop in resistivity, suggesting the onset to a metallic state. From the bulk magnetization and the transport data we could associate a larger value of T_C with a more metallic character, and a lower value of the CMR effect (Sb-doped sample). On the other hand, Cd doping leads to a sharp metal-insulator transition with a variation of 7 orders of magnitude of the resistivity (at zero magnetic field). The ferromagnetic ordering temperature is almost the same with respect to the pure compound, and presents a large CMR effect up to 99.99% (for $Tl_{1.8}Cd_{0.2}Mn_2O_7$), under an applied magnetic field of 9 T.

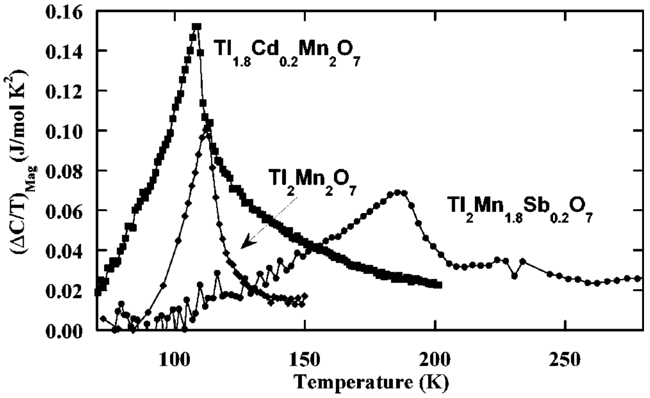

FIG. 2. Temperature dependence of the magnetic and electronic specific heat divided by T for $Tl_2Mn_2O_7$, $Tl_{1.8}$ $Cd_{0.2}Mn_2O_7$, and $Tl_2Mn_{1.8}Sb_{0.2}O_7$. The phononic component (modeled by three Einstein oscillators) is already substracted as explained in the text. The lines are a guide to the eye.

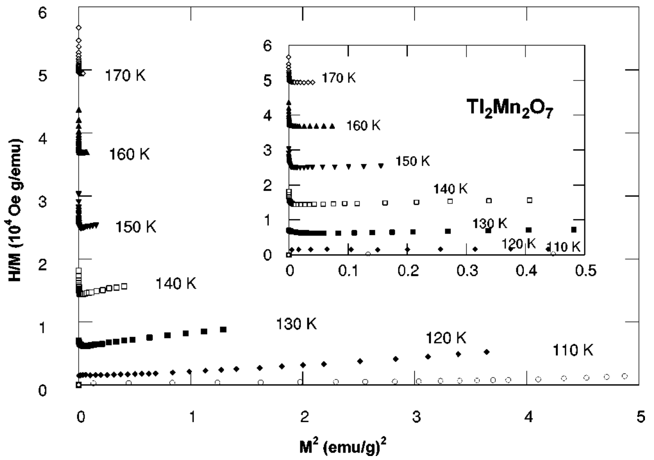

FIG. 3. H/M vs M^2 isotherms of $Tl_2Mn_2O_7$ around T_C. Note the onset, at low fields, of a negative slope at a temperature near the critical point. Inset: Detail data for smaller values of magnetization.

The temperature dependence of the thermopower (S) is presented in Fig. 1. The value of S is negative in all the temperature range for the three samples, what suggests that the charge carriers are electrons (negative Hall resistance). The value of S for $Tl_2Mn_{1.8}Sb_{0.2}O_7$ is almost 20 times smaller than for the other two compounds. The large value of S for $Tl_2Mn_2O_7$ and $Tl_{1.8}Cd_{0.2}Mn_2O_7$ is consistent with the small carrier density observed in these compounds (0.005 e^-/u.c. and 0.0002 e^-/u.c., respectively[13,15]). In all the cases a linear behavior is observed far from T_C (low and high temperatures), but a sharp increase of S around T_C is noticeable in the three compounds. This is specially strong in the case of $Tl_{1.8}Cd_{0.2}Mn_2O_7$, where a sharp peak is observed around T_C, which implies a big change in the slope dS/dT. This could be related to a sharp variation of the charge carriers density around T_C.

The specific heat data for the three compounds were measured in a wide temperature range around T_C. We are interested in the magnetic part of the specific heat, so that we need to remove the strong phononic component from the total specific heat. In order to calculate the phononic component, we use an Einstein model with three oscillators centered at three frequencies (120, 250, and 575 K). The phononic component is rather large at this temperatures, and could acount up to 80% of the signal at the peak position. The subtraction of the phononic component from the total (measured) specific heat is presented in Fig. 2 as the magnetic and electronic specific heat around T_C for the three compounds. At this temperature range the electronic component of the specific heat is considered to be very small, and only the magnetic one is significant. The data clearly show the magnetic transition although they do not assess on its character as first or second order.

In order to study the character of the magnetic phase transition we will apply pure magnetic methods, as the Banerjee criterium, explained above. Initial magnetization isotherms were measured around the respective T_C's. Before each isothermal run, samples were heated up to 300 K (well above

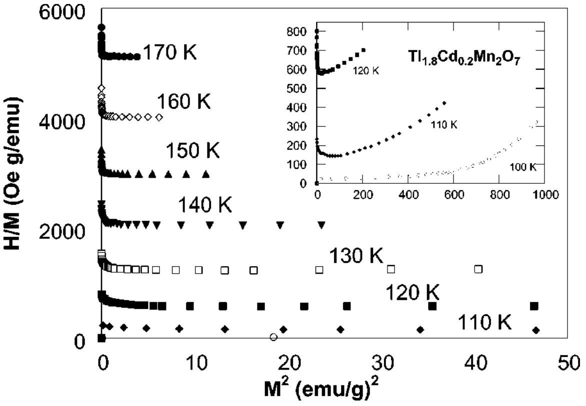

FIG. 4. Detail of the H/M vs M^2 isotherms of $Tl_{1.8}Cd_{0.2}Mn_2O_7$. As in the undoped system, the negative slope starts near T_C. The inset shows H/M vs M^2 isotherms for temperatures closer to T_C.

their T_C's) and cooled to the measuring temperature under zero field, in order to ensure perfect demagnetization of the samples.

Figure 3 shows the results for $Tl_2Mn_2O_7$. At 130 K ($\simeq T_C$), the curves show a small negative slope, indicating, according to Banerjee's criterion, a first-order character of the transition. This negative slope, found at low fields, continues above this temperature (see inset). This fact is probably causing the "unusual characteristics" found by Zhao *et al.* in the analysis of the critical behavior of the system.[5] The same happens for the Cd-substituted pyrochlore (Fig. 4), with a negative slope starting from 110 K ($\simeq T_C$), and for the Sb-substituted one (Fig. 5), where the negative slope appears at 190 K. From the above experimental data we conclude that the magnetic phase transition for the three compounds is first order. In the case of $Tl_2Mn_2O_7$ the transition is weakly first order, but for $Tl_{1.8}Cd_{0.2}Mn_2O_7$ and $Tl_2Mn_{1.8}Sb_{0.2}O_7$ is clearly first order.

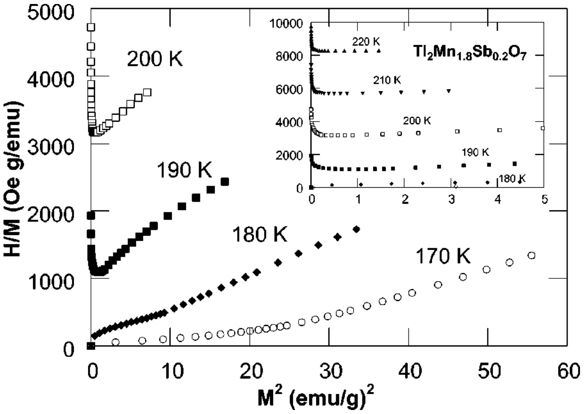

FIG. 5. H/M vs M^2 isotherms, around T_C, of $Tl_2Mn_{1.8}Sb_{0.2}O_7$. The negative slope starts at about 190 K. Inset: Detail of some isotherms at higher temperatures and expanded values of magnetization.

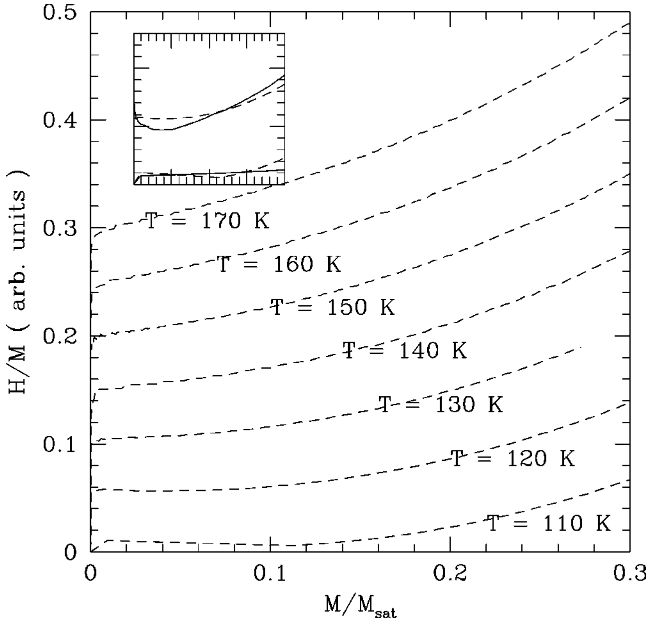

FIG. 6. Calculated values of H/M vs M^2 for the model discussed in the text. Inset: Comparison with the results for $T=110$ K and 120 K in Fig. 4. Full curves are the experimental data, and broken curves are the fittings by the model.

We assume that magnetization of the pyrochlores is determined by the Mn^{4+} ions, which interact with a dilute band of conduction electrons. There is a ferromagnetic direct interaction between the spins of the Mn ions, J, and a local Kondo-like coupling between the Mn spins and the conduction electrons J'.[8,10–12,21] The Hamiltonian can be approximated as $\mathcal{H}=\Sigma_{k,s}\epsilon_k c^{\dagger}_{k,s}c_{k,s}-J\Sigma_{ij}\vec{\mathbf{M}}_i\cdot\vec{\mathbf{M}}_j-J'\Sigma_i c^{\dagger}_{i,s}\vec{\sigma}_{ss'}c_{i,s'}\vec{\mathbf{M}}_i$ and $\epsilon_k=\hbar^2|\vec{\mathbf{k}}|^2/2m_{\rm eff}$. The magnetization of the Mn ion at site i is denoted as $\vec{\mathbf{M}}_i$ and $\vec{\mathbf{s}}_i=\Sigma_{s,s'}c^{\dagger}_{i,s}\vec{\sigma}_{ss'}c_{i,s'}$ is the polarization of the carriers at unit cell i. This Hamiltonian is characterized by three parameters with dimension of energy J,J', and the bandwidth W. The later can be written in terms of $m_{\rm eff}$ and the lattice constant a as $W=(\hbar^2\pi^2)/(2m_{\rm eff}a^2)$. In addition, we have to specify the number of conduction electrons per unit cell n or, alternatively, the position of the chemical potential μ. In the following, we will assume that n can change as function of temperature and applied field, while μ is constant, as suggested in recent experiments.[22]

The above Hamiltonian can be analyzed by a variety of methods. It can be shown, that, in the limit of a highly diluted conduction band,[12] polarons will be formed in the paramagnetic phase. The same arguments can be used to proof that the stability of isolated small polarons imply the tendency towards phase separation in the presence of a finite carrier density.[21] This result, in turn, implies that the magnetic transition becomes first order. This transition arises from the feedback of the carriers on the Mn spins.[21] The coupling of the spin of the conduction electrons to the Mn ions induces an effective interaction between the Mn spins, which goes as $-J'\vec{\mathbf{M}}\cdot\vec{\mathbf{s}}(\vec{\mathbf{M}})$. If $\vec{\mathbf{s}}(\vec{\mathbf{M}})$ changes fast enough, this coupling leads to a negative quartic term in the free energy of the Mn spins. The relative strength of this term increases as the carrier density is reduced and, when the carrier density is small enough, it overcomes the usual positive quartic term, which arises from the entropy of the Mn ions, leading to a first order phase transition.[17]

In the following, we use the mean field approach developed in Ref. 21 to study the properties of a system described by the above Hamiltonian in the presence of a magnetic field, and at constant chemical potential. The results are plotted in Fig. 6. The parameters used are $J = W/9$ and $J' = W/3$. We fit the value of $W \approx 0.4$ eV, so that $T_C \approx 110$ K. The chemical potential is $\mu = -0.05W$, and the carrier density at low temperatures is ≈ 0.05 per unit cell. We keep the chemical potential fixed. The inset shows a fitting to the results for the two lowest temperatures in Fig. 4. Note that the model includes only the bare essentials of the magnetic interactions, and it ignores effects such as disorder and spatial fluctuations. Nevertheless, it seems to reproduce qualitatively the main features of the experimental data. Finally, in real materials, phase separation at long scales will be prevented by the electrostatic energy associated with the displaced electric charges. This effect has been studied in the manganites,[21,23] where the expected domain sizes are not much larger than the unit cell. In the pyrochlores, on the other hand, the local carrier density is at least one order of magnitude lower than in the manganites. The Coulomb energy scales as the square of the induced charge inhomogeneities. Hence, fluctuations on scales much larger than the unit cell can be expected.

We conclude that the character of the magnetic phase transition in $Tl_2Mn_2O_7$ CMR pyrochlores is first order, in contrast to previous studies.[5] This first order character is compatible with a complex ordering mechanism composed of a direct superexchange interaction between Mn ions, and a local Kondo-type indirect coupling between Mn ions mediated by the low density of conduction electrons. The ordering temperature seems to be diretly related to this density of conduction electrons (i.e., the higher T_C, the higher density of carriers, as is the case for $Tl_2Mn_{1.8}Sb_{0.2}O_7$). Moreover, the CMR effect seems not to be related to the first order character of the magnetic transition, since CMR is rather weak for $Tl_2Mn_{1.8}Sb_{0.2}O_7$, which presents a clear first order character. The higher CMR is obtained when the charge carriers density is very low, and it seems to vary strongly around T_C (i.e., the case of $Tl_{1.8}Cd_{0.2}Mn_2O_7$). All these elements (first order character, variation of CMR and density of carriers) are obtained from a simple Hamiltonian solved in a mean field approximation,[21] which reproduces all of the above mentioned effects and also predicts a phase separation.

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