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Origin and pressure dependence of ferromagnetism in $A_2Mn_2O_7$ pyrochlores (A=Y, In, Lu, and Tl)

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Nonconventional mechanisms have been recently invoked in order to explain the ferromagnetic ground state of $A_2Mn_2O_7$ pyrochlores (A=Y, In, Lu, and Tl) and the puzzling decrease of their Curie temperatures with applied pressure. Here we show, using a perturbation expansion in the Mn-O hopping term, that both features can be understood within the superexchange model, provided that the intra-atomic oxygen interactions are properly taken into account. An additional coupling between the Mn ions mediated by the In($5s$)/Tl($6s$) bands yields the higher T_C's of these two compounds, this mechanism enhancing their ferromagnetism for higher pressures.

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The observation of colossal magnetoresistance (CMR) in $Tl_{2-x}In_xMn_2O_7$ pyrochlores[1–3] challenges our understanding of this phenomenon with important technological applications. In fact, in contrast with their perovskite counterparts, these systems do not present mixed Mn^{3+}-Mn^{4+} valences, they have a small number of conduction carriers ($\sim 10^{-3}$ per formula unit), and they do not exhibit Jahn-Teller effect or anomalous spin diffusion, denying both the usual double exchange and the polaronic mechanisms invoked in that case. Furthermore, in spite of the similar CMR effect observed, the magnetic transition does not occur between a low-temperature metal and a high-temperature semiconducting state like in the perovskites, but both the ferromagnetic and the paramagnetic phases show metallic behavior. These compounds belong to the larger family of $A_2Mn_2O_7$ pyrochlores, the metallic behavior of the A=Tl compound being the exception, since all other members are insulators. But they all show long-range ferromagnetic ordering and can be classified in two groups according to their transition temperatures:[4] $T_C \sim 15$ K for A=Y and Lu, while $T_C \sim 125$ K for A=In and Tl.

Considering the Mn^{4+}-O(I)-Mn^{4+} bond angle θ, a ferromagnetic superexchange picture between nearest-neighbor (NN) Mn ions has been initially suggested.[3,4] In fact, following the Goodenough-Kanamori-Anderson rules,[5] the $\theta \sim 132°$ of this pyrochlore structure falls into the range in which a sign reversal of the exchange constants is expected. Using the phenomenological approach for the angular dependence of the exchange interactions for the similar case of Cr^{3+}-O^{2-}-Cr^{3+} ions,[6] Shimakawa *et al.*[4] found a slightly ferromagnetic exchange J interaction, in agreement with the low Curie temperatures observed for $Y_2Mn_2O_7$ and $Lu_2Mn_2O_7$. Furthermore, without proposing a particular mechanism, they pointed out the possible role of the hybridization of the In($5s$)/Tl($6s$)-O($2p$)-Mn($3d$) orbitals in enhancing T_C in these two compounds.[4]

On the other hand, taking the ferromagnetic ordering as an experimental fact, different theories attempted to explain the CMR effect. Scattering against ferromagnetic fluctuations, relevant in this case with a very low number of carriers,[7] or simply hybridization of the localized moments with the itinerant Tl($6s$) states have been invoked[8] as possible mechanisms for the CMR.

However, recent measurements showing a decrease of the ferromagnetic T_C with increasing applied pressure for all $A_2Mn_2O_7$ compounds[9] have been interpreted as contradicting the original superexchange picture. The data establish that materials with lower T_C possess a larger negative pressure shift ($dT_C/dP = -3.8$, -2.5, -1.6, and -0.4 K/GPa, and $d\ln T_C/dP = -24.5$, -20.8, -11.2, and -0.3%/GPa, for A=Lu, In, Tl, and In, respectively). A more exotic scenario has been suggested with antiferromagnetic (AF) coupling between NN Mn ions overcome by longer-range ferromagnetic interactions, due to the frustration of the former in the pyrochlore lattice.[9] Also, the enhancement of the ferromagnetic coupling in Sb-substituted $Tl_2Mn_2O_7$ compounds has been discussed[10] as strongly supporting this proposal. But taking into account the structural parameters of these systems, the justification of the necessary exchange constants seems difficult.

Here we show that the observed weakening of the ferromagnetism with moderate pressures can be understood within the conventional superexchange model, provided that the intra-atomic Hund interaction J_H^O of the oxygen has a significant value, while the excitation energy Δ of the O($2p$) electrons to the empty e_g levels of the localized Mn ions is small. Comparison with other oxides should indicate that these can be reasonable assumptions. The resulting exchange interaction J is ferromagnetic due to the Mn^{4+}-O(I)-Mn^{4+} bond angle, and when an external pressure is applied, Δ increases while the intra-atomic parameter J_H^O remains unchanged, inducing the observed decrease of T_C. However, an additional mechanism is still necessary to account for the observed T_C's above 120 K. We propose a superexchange coupling between the Mn(t_{2g}) states mediated by the In($5s$)/Tl($6s$)-O($2p$) bands, which also explains the increase of T_C reported later for higher pressures.[11] Although the relevant bands become strongly spin polarized, the ferromagnetism and the conduction in the $Tl_2Mn_2O_7$ compound appear to be less coupled than in the perovskites, in agreement with experimental results.[12,13]

We now calculate the exchange interaction between two manganese ions of the pyrochlore lattice, forming an angle θ between them through an intermediate full oxygen atom O(I). Each Mn ion has an inert t_{2g} core with $s=3/2$ and, for simplification, let us consider just a single empty e_g orbital state [in fact, only the orbital directed towards O(I) is relevant], onto which an O$(2p)$ electron can hop, provided that it has the same spin orientation, e.g., the Hund's rule energy cost on the Mn ion J_H^{Mn} is taken as infinite, avoiding hops of antiparallel spins (therefore it is not necessary to include the Coulomb repulsion on the Mn ions). The O(I) ions mediate the superexchange interaction, the four $2p$ electrons moving back and forth between the O and the two NN Mn orbitals within the same plane. We call t the Mn-O(I) hopping matrix element, Δ the energy difference between the O$(2p)$ levels (p_x, p_y) and the e_g state of each Mn site (d_1, d_2), J_H^{O} is the Hund's rule energy on the O ions, and U_p the Coulomb repulsion between two holes on the same O atom. These two last parameters are of crucial importance since they will be responsible for the ferromagnetic interaction for the relevant Mn-O(I)-Mn angles θ ($\theta \sim 130.8°$, $131.4°$, $132.4°$, and $133.4°$ for $A=$ In, Lu, Y, and Tl, respectively).[4]

When the core spins of two NN Mn ions $\vec{s}_1$ and $\vec{s}_2$ are ferromagnetically aligned, the possible occupations for the parallel hopping spins (e.g., up spins) are $|d_1p_x\rangle$, $|d_1p_y\rangle$, $|d_1d_2\rangle$, $|p_xp_y\rangle$, $|p_xd_2\rangle$, and $|p_yd_2\rangle$. The corresponding Hamiltonian reads:

$$H_{\uparrow\uparrow}=\begin{pmatrix} \Delta & 0 & -t_2 & -t_1 & 0 & 0 \\ 0 & \Delta & t_1 & t_2 & 0 & 0 \\ -t_2 & t_1 & 2\Delta+U_p-J_H^{\mathrm{O}} & 0 & t_2 & t_1 \\ -t_1 & t_2 & 0 & 0 & t_1 & t_2 \\ 0 & 0 & t_2 & t_1 & \Delta & 0 \\ 0 & 0 & t_1 & t_2 & 0 & \Delta \end{pmatrix} \tag{1}$$

where $t_1 \equiv t\cos(\theta/2)$ and $t_2 \equiv t\sin(\theta/2)$, which we solve for $t/\Delta<1$ up to fourth order in the hopping element t. In previous calculations,[14] the J_H^{O} and U_p terms have been omitted, losing the contribution that can give rise to the ferromagnetic interaction. We obtain

$$E_{\uparrow\uparrow}=-\frac{2t^2}{\Delta}+\frac{2t^4[1+\cos^2(\theta)]}{\Delta^2\left(\Delta+\frac{U_p}{2}-\frac{J_H^{\mathrm{O}}}{2}\right)}+\frac{2t^4(U_p-J_H^{\mathrm{O}})}{\Delta^3\left(\Delta+\frac{U_p}{2}-\frac{J_H^{\mathrm{O}}}{2}\right)}. \tag{2}$$

Instead, when the two NN core Mn ions are antiparallel (e.g., $\vec{s}_1=$ up and $\vec{s}_2=$ down), there are three spin-up and three spin-down possible occupations for the four oxygen hopping electrons:[14] $|d_1p_x, d_2p_x\rangle$, $|d_1p_x, d_2p_y\rangle$, $|d_1p_x, p_xp_y\rangle$, $|d_1p_y, d_2p_x\rangle$, $|d_1p_x, d_2p_y\rangle$, $|d_1p_y, p_xp_y\rangle$, $|p_xp_y, d_2p_x\rangle$, $|p_xp_y, d_2p_y\rangle$, and $|p_xp_y, p_xp_y\rangle$, where now the two first indexes correspond to the spins up and those after the comma to the spins-down occupations, respectively. They yield the following Hamiltonian:

$$H_{\uparrow\downarrow}=\begin{pmatrix} 2\Delta+U_p & 0 & -t_1 & 0 & 0 & 0 & -t_1 & 0 & 0 \\ 0 & 2\Delta+U_p & -t_2 & J_H^{\mathrm{O}} & 0 & 0 & 0 & -t_1 & 0 \\ -t_1 & -t_2 & \Delta & 0 & 0 & 0 & 0 & 0 & -t_1 \\ 0 & J_H^{\mathrm{O}} & 0 & 2\Delta+U_p & 0 & -t_1 & t_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\Delta+U_p & -t_2 & 0 & t_2 & 0 \\ 0 & 0 & 0 & -t_1 & -t_2 & \Delta & 0 & 0 & t_2 \\ -t_1 & 0 & 0 & t_2 & 0 & 0 & \Delta & 0 & -t_1 \\ 0 & -t_1 & 0 & 0 & t_2 & 0 & 0 & \Delta & -t_2 \\ 0 & 0 & -t_1 & 0 & 0 & t_2 & -t_1 & -t_2 & 0 \end{pmatrix}. \tag{3}$$

We calculate again the ground-state energy up to t^4 order, obtaining

$$\begin{aligned} E_{\uparrow\downarrow}=&-\frac{2t^2}{\Delta}+\frac{2t^4}{\Delta\left[\left(\Delta+\frac{U_p}{2}\right)^2-\frac{(J_H^{\mathrm{O}})^2}{4}\right]}-\frac{t^4J_H^{\mathrm{O}}\sin^2(\theta)}{2\Delta^2\left[\left(\Delta+\frac{U_p}{2}\right)^2-\frac{(J_H^{\mathrm{O}})^2}{4}\right]}+\frac{3t^4U_p}{\Delta^2\left[\left(\Delta+\frac{U_p}{2}\right)^2-\frac{(J_H^{\mathrm{O}})^2}{4}\right]} \\ &-\frac{t^4(J_H^{\mathrm{O}})^2\sin^2(\theta)}{4\Delta^2\left(\Delta+\frac{U_p}{2}\right)\left[\left(\Delta+\frac{U_p}{2}\right)^2-\frac{(J_H^{\mathrm{O}})^2}{4}\right]}+\frac{t^4[2(U_p)^2-(J_H^{\mathrm{O}})^2]}{2\Delta^3\left[\left(\Delta+\frac{U_p}{2}\right)^2-\frac{(J_H^{\mathrm{O}})^2}{4}\right]}-\frac{t^4(J_H^{\mathrm{O}})^2U_p}{4\Delta^3\left(\Delta+\frac{U_p}{2}\right)\left[\left(\Delta+\frac{U_p}{2}\right)^2-\frac{(J_H^{\mathrm{O}})^2}{4}\right]}. \end{aligned} \tag{4}$$

The difference of the leading eigenvalues is

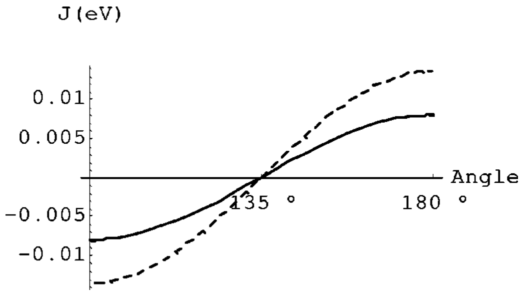

FIG. 1. Angle dependence of the NN Mn-O(I)-Mn exchange interaction J, Eq. (5), for typical parameters: $J_H^{\mathrm{O}}=0.8$ eV, $U_p=1$ eV, $\Delta=0.1$ eV. Continuous (dashed) curve: $t=0.07$ eV ($t=0.08$ eV).

$$J=E_{\uparrow\uparrow}-E_{\uparrow\downarrow}=\frac{2t^4\cos^2(\theta)}{\Delta\left[\left(\Delta+\frac{U_p}{2}\right)^2-\frac{(J_H^{\mathrm{O}})^2}{4}\right]}+\frac{t^4\left[U_p\cos^2(\theta)-\left(\frac{J_H^{\mathrm{O}}}{2}\right)\sin^2(\theta)\right]}{\Delta^2\left[\left(\Delta+\frac{U_p}{2}\right)^2-\frac{(J_H^{\mathrm{O}})^2}{4}\right]}-\frac{t^4(J_H^{\mathrm{O}})^2[2-\sin^2(\theta)]}{4\Delta^2\left(\Delta+\frac{U_p}{2}\right)\left[\left(\Delta+\frac{U_p}{2}\right)^2-\frac{(J_H^{\mathrm{O}})^2}{4}\right]}. \tag{5}$$

Thus, to the AF result of Ref. 14 are added now other terms, which, depending on the Δ, J_H^{O}, and U_p values, can yield a ferromagnetic coupling for the bond angle of these pyrochlores, without the necessity of invoking more complicated mechanisms.[14] As expected, J_H^{O} must have a significant value, as is the case for other oxides in which this parameter also induces a ferromagnetic interaction, e.g., $\mathrm{NaNiO_2}$ with $\theta\sim95°$ for NN Ni ions within the same layer.[15] For $\theta=135°$, the condition is

$$J_H^{\mathrm{O}}>\frac{4}{3}\left(\Delta+\frac{U_p}{2}\right), \tag{6}$$

which means that the O($2p$) levels must be close to the Mn(e_g) state. In Fig. 1, we plot the angular dependence of Eq. (5). To our knowledge, there are not yet photoemission experiments nor constrained calculations yielding these energies for the $A_2\mathrm{Mn_2O_7}$ pyrochlores. Therefore, we take the conventional wisdom for U_p and J_H^{O} (Refs. 5 and 16) (values somewhat smaller than for the Mn ions in the CMR perovskites[17]), and we derive the Δ and t parameters necessary to reproduce the observed critical temperatures for $A=\mathrm{Y}$ and Lu.

This first calculation shows that the superexchange alone can explain the ferromagnetic ordering of these compounds at ~15 K. Furthermore, the observed decrease of T_C with pressure, inducing an isomorphic reduction of the lattice parameters,[11] appears as a confirmation of this mechanism: the directional e_g levels of the Mn ions will go up in energy, and instead, the intra-atomic J_H^{O} will not significantly change. Figure 2 shows the change of the exchange interaction J with Δ, which is an increasing parameter with the applied pressure. We can see in Fig. 3 that, for the angles relevant to these pyrochlores, the resulting ferromagnetic interaction can decrease, even if there is a simultaneous increase of the Mn-O(I) hopping t.

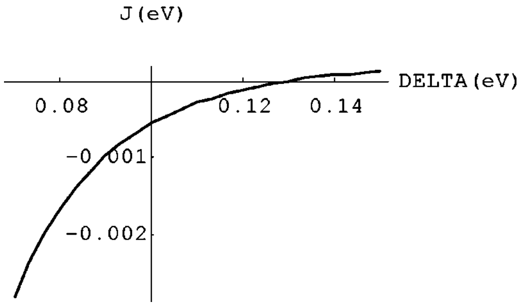

FIG. 2. Variation of J with the energy difference Δ between O($2p$) levels and the Mn(e_g) states, given by Eq. (5), for $J_H^{\mathrm{O}}=0.8$ eV, $U_p=1$ eV, $t=0.07$ eV, and $\theta=133°$.

However, the systematic study performed by Shimakawa *et al.*[4] provides evidence that there is an additional feature determining T_C, since the $A=\mathrm{In}$, Tl compounds, with similar Mn-O distances and angles to those of $A=\mathrm{Y}$, Lu, have both $T_C\sim125$ K. The important difference between both groups of pyrochlores is the nature of the A atom surrounded by inequivalent oxygen ions [we call O(II) the closer ones], that is reflected in the corresponding band structures.[4] For the Y compound, the first unoccupied states correspond to the Mn(e_g) levels, the Y-O(II)-O(I) states having higher energies. Then the only relevant mechanism is the one calculated before, yielding $T_C\sim15$ K.

In contrast, the In($5s$)- and Tl($6s$)-O(II)-O(I) bands are lower in energy and strongly hybridized with the empty e_g orbital.[18] Therefore, the t_{2g} electrons can go to these states of energy Δ' (we call t' the corresponding matrix element) and due to the large J_H^{Mn}, this hopping will induce a strong ferromagnetic interaction J' between the Mn ions. We can estimate[17]

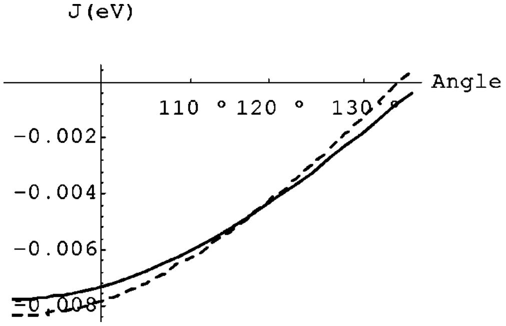

FIG. 3. Variation of J with the simultaneous increase of Δ and the Mn-O(I) hopping t. Continuous curve: $\Delta=0.08$ eV, $t=0.06$ eV. Dashed curve: $\Delta=0.12$ eV, $t=0.08$ eV.

$$J' \simeq 0.8T_C \simeq \frac{t'^2}{\Delta'} \sim 100\ \mathrm{K}, \tag{7}$$

which yields $t' \sim 0.14$ eV for $\Delta' \sim 2$ eV.[4] The majority-spin empty band will be strongly polarized parallel to the moment of the Mn ions.

On the other hand, we can understand why the conduction band in $Tl_2Mn_2O_7$ is strongly polarized in the opposite direction: it will lower its energy by hybridization with the O(I) states that do not participate in the superexchange ferromagnetic coupling.

In those cases, in which the conduction band approaches (as in $A=$In) or crosses the Fermi level (for $A=$Tl), we expect a relatively smaller decrease of the critical temperature (as observed[9]) and even a rise of T_C for higher pressures when these bands are modified, further lowering their energies. Recent measurements[11] confirm this change of tendency for $Tl_2Mn_2O_7$, i.e., they show an initial decrease followed by an increase of T_C with applied pressure, the minimum critical temperature corresponding to ~ 1 GPa. We expect a similar behavior for $A=$In without an enhanced change in the magnetism due to the eventual insulator-metal transition induced by higher pressure. The increase of the ferromagnetic coupling in $Tl_2(Mn_{2-x}Sb_x)O_7$ (the Sb substitution acting as a negative pressure) can be understood within the same picture, more easily than considering[10] an AF superexchange coupling between NN Mn ions.

We conclude that when the oxygen intra-atomic interactions are properly included in the calculations, the superexchange between NN Mn ions suffices to explain the ferromagnetic T_C's$\sim$15 K of $A_2Mn_2O_7$ pyrochlores, as well as their decrease with applied pressure. Instead, an additional mechanism involving the In($5s$)/Tl($6s$)-O($2p$)-Mn(e_g) bands and the t_{2g} electrons is necessary to account for the higher T_C's$\sim$125 K and their nonmonotonic behavior with pressure.

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