Spin dynamics in perovskites, pyrochlores, and layered manganites

S. B. Oseroff, N. O. Moreno, P. G. Pagliuso, C. Rettori, D. L. Huber, J. S. Gardner, J. L. Sarrao, J. D. Thompson , M. T. Causa, G. Alejandro, M. Tovar, and B. R. Alascio

---

Articles you may be interested in

Tunable spin reorientation transition and magnetocaloric effect in Sm0.7−xLaxSr0.3MnO3 series
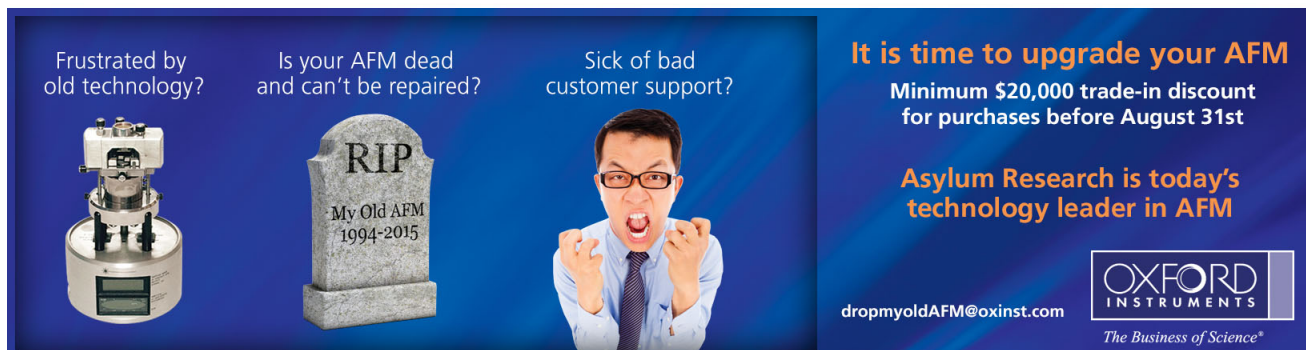J. Appl. Phys. **113**, 013911 (2013); 10.1063/1.4773337

Spin dynamics and spin-glass state in Fe-doped cobaltites
J. Appl. Phys. **95**, 7531 (2004); 10.1063/1.1667442

Spin–lattice interaction in colossal magnetoresistance manganites
Appl. Phys. Lett. **77**, 4025 (2000); 10.1063/1.1329324

Strain-dependent magnetic phase diagram of epitaxial La 0.67 Sr 0.33 MnO 3 thin films
Appl. Phys. Lett. **76**, 2421 (2000); 10.1063/1.126363

Pyrochlore manganites spin dynamics in the paramagnetic regime
J. Appl. Phys. **85**, 5408 (1999); 10.1063/1.369993

Spin dynamics in perovskites, pyrochlores, and layered manganites

S. B. Oseroff[a)]
San Diego State University, San Diego, California 29182-8062

N. O. Moreno, P. G. Pagliuso, and C. Rettori
Instituto de Física ''Gleb Wataghin,'' UNICAMP, Campinas, Sao Paulo 13083-970, Brazil

D. L. Huber
University of Wisconsin-Madison, Madison, Wisconsin 53706

J. S. Gardner, J. L. Sarrao, and J. D. Thompson
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

M. T. Causa, G. Alejandro, M. Tovar, and B. R. Alascio
*Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica
and Universidad Nacional de Cuyo, 8400 San Carlos de Bariloche, Argentina*

High temperature electron spin resonance (ESR) and magnetic susceptibility (χ) are analyzed for manganites related with colossal magnetoresistance (CMR). The properties of compounds with different crystalline structures: three-dimensional (3D) perovskites, pyrochlore, and $La_{1.2}Sr_{1.8}Mn_2O_7$, a two-dimensional layer, are compared. In the paramagnetic regime, and outside the critical regions associated with phase transitions, the temperature dependence of the ESR linewidth presents a universal behavior dominated by the variations of $\chi(T)$, $\Delta H_{pp}(T) = [C/T\chi(T)]\Delta H_{pp}(\infty)$. The high temperature limit of the linewidth, $\Delta H_{pp}(\infty)$, is related to the parameters of the Hamiltonian describing the interactions of the spin system. The role played by magnetic anisotropy, isotropic superexchange, and double exchange is revealed and discussed in the analysis of the experimental data. In CMR and non-CMR pyrochlores, $\Delta H_{pp}(\infty) \propto \omega_p^2/J$ where J is proportional to the Curie–Weiss temperature, including the hybridization mechanism producing CMR. Instead, $\Delta H_{pp}(\infty)$ of CMR perovskites seems not to be affected by the double-exchange interaction. In contrast with the 3D perovskites, the ESR linewidth and resonance field of $La_{1.2}Sr_{1.8}Mn_2O_7$, a bilayer compound, although isotropic at high temperatures, becomes anisotropic for $T_c = 125\,K < T < T_p \approx 450\,K$. © *2000 American Institute of Physics.* [S0021-8979(00)42308-X]

The goal of this work is to study the magnetic properties of colossal magnetoresistance (CMR) oxides in the paramagnetic phase and compare them with compounds of the same family that do not show CMR. Results for a variety of three-dimensional (3D) perovskites $La_{1-x}Ca_xMnO_3$ and pyrochlores $A_2Mn_2O_7$ (A=Y, In, and Tl) manganites have been analyzed. In addition, $La_{1.2}Sr_{1.8}Mn_2O_7$, a layered manganite was also studied.

By performing electron spin resonance (ESR) and dc susceptibility measurements up to 1000 K, the temperature dependence of the ESR linewidth, ΔH_{pp}, has been investigated.[1,2] It was found that for all the 3D compounds (perovskites and pyrochlores), the ESR linewidth, outside critical regions associated with structural and magnetic phase transitions, can be described by the expression

$$\Delta H_{pp}(T) = [C/T\chi(T)]\Delta H_{pp}(\infty), \tag{1}$$

where $\chi(T)$ is the dc susceptibility and $\Delta H_{pp}(\infty)$ is the linewidth expected at temperatures high enough for the dc susceptibility to follow a Curie–Weiss (CW) law. A universal behavior for $\Delta H_{pp}(T)$ was found, where the only free parameter is $\Delta H_{pp}(\infty)$ when T is normalized to the critical temperature, T_c, or the Curie–Weiss temperature, Θ. The whole T dependence is contained in the term $[C/T\chi(T)]$ and no evidence of a spin–phonon contribution to the ΔH_{pp} was found. Thus, in this regard there is no difference between CMR and non-CMR compounds. Our data show that one must go to at least $3T_c$ to establish the limiting behavior at high temperatures that is reflected in Eq. (1).[1,2] Previous data for $\Delta H_{pp}(T)$ were taken between $T_c < T < \sim 2T_c$, a region where temperatures $\chi(T)$ does not follow a Curie–Weiss law.[1]

It can be shown that interesting physics is contained in $\Delta H_{pp}(\infty)$. As pointed out by Anderson and Weiss,[3] the ESR lines are exchange narrowed with $\Delta H_{pp}(\infty) \propto (\omega_p)^2/J$, where ω_p takes into account the anisotropic spin interactions (dipolar interactions, low symmetry crystal field, and anisotropic and antisymmetric exchange, etc.) and the isotropic exchange constant J is proportional to Θ. In Table I, values of Θ for CMR and non-CMR are given within the same series. The values of Θ are larger for the CMR systems as a result of the intense ferromagnetic (FM) interaction present in these compounds. For the perovskite compounds a double-exchange mechanism[4] (DE) is the origin of the FM and CMR effect. Shimakawa *et al.*[5] have recently discussed the magnetic properties and the electronic band structure for compounds with pyrochlore structure. They concluded that the ferromagnetic behavior observed on them is compatible

a)Electronic mail: soseroff@sciences.sdsu.edu

TABLE I. $\Delta H_{pp}(\infty)$ and CW temperature for manganites with different crystalline structures.

Compound	Crystal structure	$\Delta H_{pp}(\infty)$ (G)	Θ (K)
$LaMnO_3$	Perovskite	2600	220
$La_{0.67}Ca_{0.33}MnO_3$	Perovskite[a]	2400	370
$La_{0.5}Ca_{0.5}MnO_3$	Perovskite	1600	250
$CaMnO_3$	Perovskite	1050	350
$Tl_2Mn_2O_7$	Pyrochlore[a]	400	170
$In_2Mn_2O_7$	Pyrochlore	500	145
$Y_2Mn_2O_7$	Pyrochlore	1830	40
$La_{1.2}Sr_{1.8}Mn_2O_7$	Layered perovskite[a]	1750	295

[a]CMR materials.

FIG. 2. $\Delta H_{pp}(T)$ vs T for $La_{1.8}Sr_{1.2}Mn_2O_7$. Open (solid) circles are for $H//c(H//a)$. Lines are fits to Eq. (1). Dotted (continuous) lines correspond to $H//c(H//a)$. Inset:$\chi^{-1}(T)$ vs T.

with a superexchange interaction between the Mn^{4+} spins, in agreement with the Goodenough–Kanamori rules. In the case of $Tl_2Mn_2O_7$, the only metallic material, a hybridization between the $Tl(6s)$ orbital and the $O(2p)$ and $Mn(3d)$ is probably the reason for the high FM transition temperature, the metallic behavior and the CMR effect[6] observed.

The experimental values of $\Delta H_{pp}(\infty)$, derived from Eq. (1), are also given in Table I. For compounds with the same structure and comparable lattice parameters similar values for ω_p are expected. Indeed, for the pyrochlores studied a single value for ω_p was obtained in Ref. 2. For 3D perovskites of the series $La_{1-x}Ca_xMnO_3$, an expression for $\Delta H_{pp}(\infty)$ was derived in Ref. 7 where ω_p was attributed primary to a Dzyaloshinkii–Moriya (DM) antisymmetric exchange contribution $\mathbf{D} \cdot \mathbf{S_i} \times \mathbf{S_j}$, and an expression $(\omega_p)^2 \propto [S(S+1)]^{1/2} D^2$ was derived, where S is the average spin. D was found basically constant[7] over the whole series, $D/k_B \approx 0.8$ K. Since the proportion of Mn^{3+}/Mn^4 (and the average spin) changes monotonically along the series, a variation of $\omega_p \approx 25\%$ is expected. Consequently, when comparing compounds within each family, one expects that the CMR materials, with larger values of Θ (and J), will have a narrower linewidth than non-CMR compounds. In Fig. 1 we plot $\Delta H_{pp}(\infty)$ vs Θ, and fits of the data to $(\omega_p)^2/J$ where we assume $\Theta = (2/3)zS(S+1)J/k_B$. For the pyrochlores the fit is excellent including CMR and non-CMR compounds. In
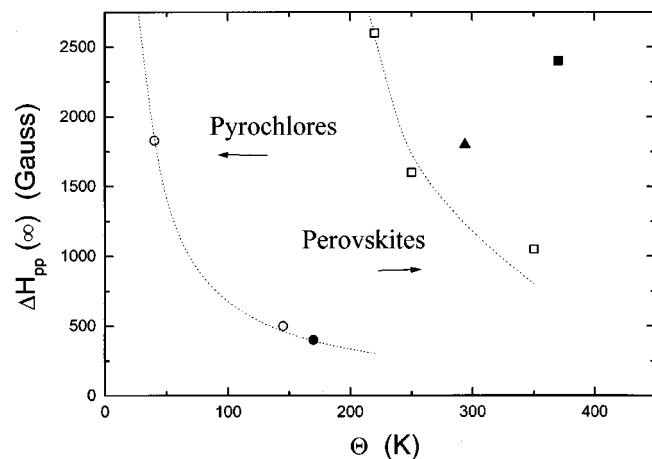
contrast, in the perovskites a good agreement is found only for the non-CMR materials. For CMR $La_{0.67}Ca(Sr)_{0.33}MnO_3$ $\Delta H_{pp}(\infty)$ is much larger than predicted by the usual exchange narrowing mechanism. This may be related to the mechanisms producing the CMR effect in each family of compounds. In pyrochlores itinerant electrons are the origin of the metallicity and CMR of $Tl_2MnO_2O_7$. In the $La_{1-x}Ca_xMnO_3$ perovskites, insulators in the paramagnetic (PM) phase, CMR originate in the DE interaction that arises from the hopping of the e_g electrons and their related lattice distortion (e_g polarons) between Mn ions. The behavior of $\Delta H_{pp}(\infty)$ for the CMR $La_{1-x}Ca(Sr)_xMnO_3$ compounds, can be contrasted with the variation of Θ, which has a peak in the neighborhood of $x = 1/3$, the concentration associated with the highest Curie T. The maximum in the Curie T is a consequence of DE. The question then arises why DE does not have a similar effect on ΔH_{pp}. It has been proposed by Huber et al.[7] that the apparent lack of an effect of DE on $\Delta H_{pp}(\infty)$ is due to the time scale associated with the changes in the Mn valence arising from DE. This is too long to influence the decay of the correlation function, whose time integral determines $\Delta H_{pp}(\infty)$. That is, if the correlation function, whose time integral determines $\Delta H_{pp}(\infty)$, decays rapidly in comparison with the time scale for significant charge redistribution, then, to a first approximation, it will be unaffected by DE. When this happens, the decay of the correlation function will be determined primarily by the superexchange interaction between the Mn ions.[7]

It is interesting to include in the analysis the results obtained for $La_{1.2}Sr_{1.8}Mn_2O_7$. The structure of this quasi-two-dimensional phase is derived from the 3D perovskite by inserting $(LaSr)_2O_2$ sheets every two MnO_2 layers. It shows a FM metallic ground state below $T_c = 125$ K and CMR.[8,9] We have measured $\chi(T)$ for single crystals with the magnetic field, $H = 3$ kG, oriented parallel and perpendicular to the MnO_2 layers: $H\|a$ and $H\|c$, respectively (see inset of Fig. 2). Above ≈ 550 K, χ follows an isotropic paramagnetic CW law with $C = 2.77$ emu K/mol Mn and $\Theta = 295$ K. We have found for $La_{1.2}Sr_{1.8}Mn_2O_7$ that M/H remains almost isotro-

FIG. 1. $\Delta H_{pp}(\infty)$ vs Θ for perovskites (squares), pyrochlores (circles), and $La_{1.2}Sr_{1.8}Mn_2O_7$ (triangle). Open and solid symbols correspond to non-CMR and CMR compounds.
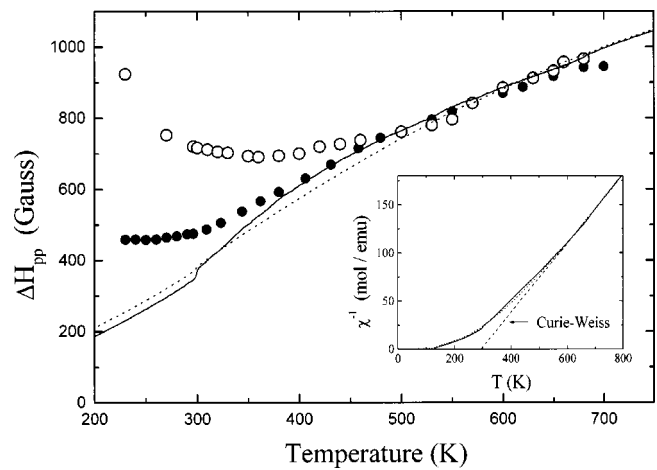
pic (for $H=3$ kG) down to $T_c=125$ K. In the PM regime ($T>T_p\sim450$ K) a dysonian ESR line with $g=2$ was obtained for all the crystals studied. Its integrated intensity has been found to follow the T dependence of $\chi(T)$ as previously reported for $La_{1.35}Sr_{1.65}Mn_2O_7$.[8] This result indicates that all Mn spins contribute to the measured line. The temperature variation $\Delta H_{pp}(T)$ is shown in Fig. 2. Above T_p the linewidth is isotropic and may be described using Eq. (1) with $\Delta H_{pp}(\infty)=1750$ G. This value is compared in Fig. 1 with the other studied compounds. A comparison with other bilayer manganites is not possible at this time because there are not available data. However, an analogy with 3D non-CMR perovskites with similar Θ values suggests that the DE mechanism, at least for $La_{1.2}Sr_{1.8}Mn_2O_7$ is relatively ineffective for the exchange narrowing of the ESR spectrum, as for the 3D perovskites. For $T<T_p$, the resonant field of the ESR line shifts to lower (or higher) fields when $H\|a$ (or $H\|c$) indicating the presence of some magnetic ordering.[9] This anisotropy is independent of the sample studied. Simultaneously, the linewidth becomes strongly anisotropic as shown in Fig. 2 and important deviations from Eq. (1) are found for $T<T_p$. For $T<370$ K, new highly anisotropic FM resonance (FMR) modes are observed. Their intensity, number, and temperature where they are first observed varies widely between crystals.[9] Thus, the FMR modes are due to the presence of extrinsic phases and not to intrinsic effects as it has been previously claimed.[8] Hence, in the PM region, above T_p, the behavior of $La_{1.2}Sr_{1.8}Mn_2O_7$ is similar to that found in 3D perovskites. However, differences appear for $T_c<T<T_p$ where a complex and highly anisotropic behavior is observed.

[1] M. T. Causa, Phys. Rev. B **58**, 3233 (1998). Measurements in $La_{1-x}Sr_xMnO_3$ were carried out by Lofland *et al.*, Phys. Lett. A **233**, 476 (1997) over the range from T_c to $2T_c$. They report quasilinear temperature dependence. Our data show that one must go to at least $3T_c$ to establish the limiting behavior at high temperatures that is reflected in Eq. (1).

[2] M. T. Causa, G. Alejandro, M. Tovar, P. G. Pagliuso, C. Rettori, S. B. Oseroff, and M. A. Subramanian, J. Appl. Phys. **85**, 5408 (1999).

[3] P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 269 (1953).

[4] C. Zener, Phys. Rev. **82**, 403 (1951).

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

[6] C. Ventura and B. Alascio, Phys. Rev. B **56**, 14 533 (1997).

[7] D. L. Huber, G. Alejandro, A. Caneiro, M. T. Causa, F. Prado, M. Tovar, and S. B. Oseroff, Phys. Rev. B **60**, 12 155 (1999).

[8] O. Chauvet, G. Goglio, P. Molinie, B. Corraze, and L. Brohan, Phys. Rev. Lett. **81**, 1102 (1998), and references therein.

[9] N. O. Moreno, P. G. Pagliuso, C. Rettori, J. S. Gardner, J. L. Sarrao, J. D. Thompson, A. García-Flores, and S. B. Oseroff (unpublished).