

## EPR and Magnetic Properties of the $\text{Ca}_n\text{Fe}_2\text{Mn}_{n-2}\text{O}_{3n-1}$ Perovskite Related Series

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**Abstract:** We present EPR and Susceptibility measurements performed on the perovskite-like family  $\text{Ca}_n\text{Fe}_2\text{Mn}_{n-2}\text{O}_{3n-1}$ . On going from  $n=2$  to  $n=3$   $\text{Fe}^{3+}$  is progressively replaced by  $\text{Mn}^{4+}$ . As a consequence the ordering temperature is depressed and frustrations in the magnetic interactions were found. The measurements are compared with the previously studied system  $\text{Ca}_n\text{Fe}_2\text{Ti}_{n-2}\text{O}_{3n-1}$  where magnetic  $\text{Mn}^{4+}$  were replaced by non magnetic  $\text{Ti}^{4+}$ . We discuss the results in terms of cationic ordering and super exchange interactions.

### 1. INTRODUCTION

The non-stoichiometric perovskites  $\text{A}_n\text{B}_n\text{O}_{3n-1}$  present a rich phenomenology which depend of the A and B cations as well as the particular ordering of the oxygen vacancies. If the cations are magnetic ions it is possible to find new magnetic properties, different of those of the "mother compound". It is the case of the series  $\text{Ca}_n\text{Fe}_2\text{Ti}_{n-2}\text{O}_{3n-1}$ , where the B site is shared by magnetic  $\text{Fe}^{3+}$  and non magnetic  $\text{Ti}^{4+}$  [1]. In this series the Oxygen polyhedrons surrounding the B cations are octahedral (Oc) or tetrahedral (Te). The O-vacancies are ordered so that in each (100) plane there is only one kind of polyhedron forming a structure of (n-1) planes Oc followed by one plane Te. The case  $n = \infty$  corresponds to the perovskite structure where all the B sites have octahedral Oxygen coordination. A decrease of the magnetic dimensionality was found on going from the compound with  $n = 2$  to the compounds with  $n=3$  or  $n=4$ , which was explained [1] taking into account the cationic ordering proposed for the system. In the present work we study the isostructural series  $\text{Ca}_n\text{Fe}_2\text{Mn}_{n-2}\text{O}_{3n-1}$  [2] where the B sites are shared for the magnetic ions  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$ .

### 2. EXPERIMENTAL PROCEDURES AND RESULTS

Sample preparation and characterization by X-ray and electron diffraction microscopy were reported in [2]. The EPR spectra were obtained at 9.5 GHz in the temperature range 100 K - 600 K. As in some spectra of  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$  the magnitude of the linewidth ( $\Delta H_{pp}$ ) is larger than the resonance field ( $H_r$ ) then the contribution of the resonance line centered at negative fields cannot be neglected. In these cases numerical simulations of the spectra were performed in order to obtain the different parameters. The EPR line intensity  $I(T)$  was obtained by double integration of the detected spectra, which are the derivatives of the absorptions. Susceptibilities  $\chi(T)$  were measured with a Faraday balance magnetometer between 60 K and 400 K.

Susceptibility measurements indicate that  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$  is a paramagnet with strong antiferromagnetic correlations in the studied T-range. For this reason neither the Curie constant nor the Curie-Weiss temperature are reported. For  $\text{CaMnO}_3$  a maximum in  $\chi(T)$  was detected indicating antiferromagnetic ordering at  $T_N = 125$  K. A weak-ferromagnetic component starts its development at this temperature, with a final magnitude which is dependent on the Oxygen stoichiometry [3].

In all the cases the EPR spectra show a single lorentzian line. In Fig. 1 we show the temperature dependence of  $H_r$  and  $\Delta H_{pp}$ . We measured  $g = 1.98(3)$  for  $\text{CaMnO}_3$ . The g-factor for  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$  was near 2, except for some shift at low temperatures. The linewidth of  $\text{CaMnO}_3$  is approximately constant with T. The absence of anomalies in the neighborhood of a critical transition was also observed in other antiferromagnetic compounds with simple cubic magnetic lattice, which was attributed to the low anisotropy associated to this structure. As is shown in Fig. 2,  $I(T)$  is Curie-like and diminishes rapidly at  $T \cong T_N$ , below which the paramagnetic mode is no longer excited. The EPR behavior of  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$  is more complex.  $\Delta H_{pp}$  shows two different regions: below and above 200 K. For  $T > 200$  K slow variations in the linewidth are observed up to 600 K, our experimental limit, well above any critical temperature. Similar behavior was observed in other magnetic compounds in which frustrations prevent a high temperature ordering. Below 200 K the linewidth shows a divergent behavior, probably due to fluctuations associated to the onset of a new magnetic state. The differences with the  $\text{CaMnO}_3$  case would indicate

important anisotropic interactions in  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$ . The existence of some degree of magnetic ordering at  $T < 200$  K can be inferred from the intensity measurements of Fig.2.  $I(T)$  is Curie-like and stop to grow at  $\approx 200$  K and, unlike the  $\text{CaMnO}_3$  case, decreases slowly for lower  $T$ . However, no indication of magnetic ordering was seen in the susceptibility for  $T \geq 60$  K. As only single spins contribute to the observed EPR line the  $I(T)$  dependence can be explained if short-range ordering is taking place. The  $g$ -shift observed at low temperatures would also be a consequence of partial magnetic ordering.

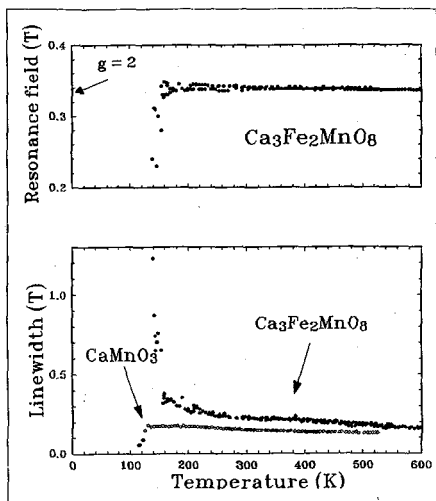


Figure 1. Resonance field and Linewidth vs. T

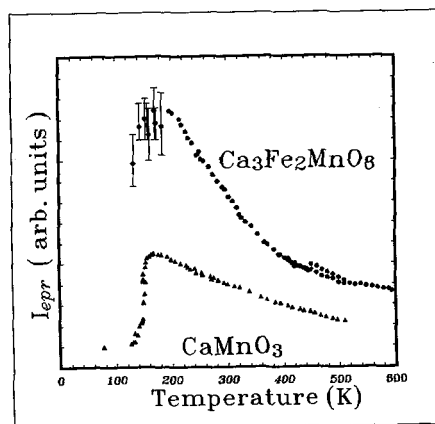


Figure 2. EPR line intensity vs. T

### 3. DISCUSSION

The extreme compounds of the series  $\text{Ca}_n\text{Fe}_2\text{Mn}_{n-2}\text{O}_{3n-1}$  are antiferromagnetic with  $T_N \approx 730$  K ( $\text{Ca}_2\text{Fe}_2\text{O}_5$ ,  $n=2$  [1]) and  $T_N \approx 125$  K ( $\text{CaMnO}_3$ ,  $n=\infty$ ). The intermediate  $n=3$  compound,  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$ , does not show ordering between these temperatures. This confirms early results [4] on perovskites  $\text{La}_{1-x}\text{M}_x\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$  ( $M=\text{Ca}, \text{Sr}$ ) which were interpreted in terms of a ferromagnetic exchange interaction between  $\text{Fe}^{3+}$ - $\text{Mn}^{4+}$  ( $J_{\text{FeMn}}/k_B \approx 15$  K). Unlike the  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$  case, no frustration were reported in those perovskites. Therefore the observed frustration could be related to the cationic ordering proposed for  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$  [2]: the Te planes are occupied by  $\text{Fe}^{3+}$  and the Oc planes are occupied by  $\text{Mn}^{4+}$  and  $\text{Fe}^{3+}$  (in equal proportion). If this is the case the Te planes would be antiferromagnetically ordered with a high exchange constant  $J_{\text{FeFe}}/k_B \approx -30$  K [1] and the Oc planes would become ferromagnetically ordered at a lower temperature. In the case  $\text{Ca}_3\text{Fe}_2\text{TiO}_8$ , magnetic ordering in the tetrahedral lattice was evidenced by EPR experiments at  $T_0 = T(I_{\text{max}}) = 330$  K. The ratio  $r = k_B T_0 / J \approx 11$  for a spin  $S=5/2$  suggested a magnetic ordering closer to that of 1D systems. This is in agreement with the occupancy of the tetrahedral sites by Fe ions because in this case each ion has only two near neighbors in the Te lattice with Fe-O-Fe bonds favorable to superexchange. With similar arguments, in the case  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$ , we obtain  $r \approx 200/15 \approx 13$  which is close to  $r = 12$ , the ratio expected for 2D ordering with  $S = 2$  (average of  $S$  in the Oc planes). In conclusion, in  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$  as in  $\text{Ca}_3\text{Fe}_2\text{TiO}_8$ , magnetic frustrations seem to be originated in the low dimensionality of the magnetic lattices which are unable to establish long range magnetic order in temperatures where  $J$  is effective. It is worth to mention that other interactions can be playing important roles. Actually, it was reported [5] that a 10 % substitution of  $\text{Mn}^{3+}$  for  $\text{Mn}^{4+}$  and  $\text{Fe}^{3+}$  in the  $n=3$  structure is the main cause for lattice disorder and spin-glass like behavior with freezing temperatures of 100 K. In our case a maximum of 3% of  $\text{Mn}^{3+}$  was detected by chemical analysis [2]. Finally, a total description of this interesting magnetic system requires susceptibility measurement covering a wider range of temperatures.

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