MAGNETIC PROPERTIES
OF Ga-DOPED LANTHANUM MANGANITE
WITH CONTROLLED OXYGEN STOICHIOMETRY

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Abstract

Stoichiometric $LaMnO_3$ is an insulator whose A-type antiferromagnetic structure at low temperature is mainly connected to the Jahn-Teller distortion of the MnO_6 octahedra. The substitution of non magnetic d^{10} Ga^{3+} ions on the manganese site disrupts the orbital and spin orderings of the manganese ions and has a strong influence on the physical properties. The antiferromagnetic order is progressively destroyed while the ferromagnetic component increases. At the same time, the distortion of the orthorhombic cell decreases and the high temperature structural Jahn-Teller transition disappears. Such studies on manganese site substitutions give insight into the physics of the Mn-O three-dimensional network, which is supposed to be the key feature in the CMR manganites.

Keywords : magnetic properties, metal oxides, perovskite

1. Introduction

Since the early nineties [1,2], there has been a renewed interest for rare earth manganites with perovskite structure, due to the discovery of Colossal MagnetoResistance (CMR) in some compounds of that family. The large drop of the electrical resistance upon application of a magnetic field could have potential applications (for example in magnetic sensors or in computer memory systems) [3] and these materials have attracted considerable attention and research. CMR usually occurs in compounds with formula $Ln_{1-x}A_xMnO_{3+/-\delta}$, where Ln is a lanthanide, A is generally an alkaline-earth and manganese has a mixed oxidation state Mn^{3+}/Mn^{4+}. Since many different cations can be substituted either on the Ln or on the Mn site, a large amount of experimental data is now available [4] and it turns out that the three-dimensional manganese oxygen network (made up of corner-sharing MnO_6 octahedra) is probably a key feature of the physics of manganites. In CMR $Ln_{1-x}A_xMnO_{3+/-\delta}$ compounds, two fundamendal parameters were identified : the Mn^{3+}/Mn^{4+} ratio (= charge carrier density) and the Mn-O-Mn orbital overlapping. The double exchange (DE) model proposed in the fifties by C. Zener [5] can qualitatively explain the CMR effect but fails to yield valid quantitative predictions.

In order to probe the exact role of the Mn-O network, it is very interesting to substitute the manganese site of the manganite perovskites. Two approaches are possible : either substitution both on the Ln and the Mn site ($Ln_{1-x}A_xMn_{1-y}B_yO_{3+/-\delta}$), or substitution only on the

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Mn site ($LnMn_{1-y}B_yO_{3+/-\delta}$). In the first case [6-8], the effect of the Mn site substitution is studied in the double exchange background induced by the Ln site substitution. In the second case [9-11], the doping cation interferes with the superexchange interactions present in the $LnMnO_3$ parent compounds.

In this work we have chosen to study the gallium substitution on the manganese site of $LaMnO_3$. Since gallium has the same 3+ charge as manganese in $LaMnO_3$, no Mn^{4+} appearance is induced by the doping and double exchange Mn^{3+}/Mn^{4+} interactions do not have to be considered. However Ga^{3+} is a d^{10} ion and this will strongly affect the physical properties : the full d orbitals are likely to disrupt the orbital and spin orderings that are present in $LaMnO_3$.

Some experimental results on the $LaMn_{1-x}Ga_xO_3$ solid solution have already been published, especially by Goodenough et al [12,13]. The originality of this work comes from the synthesis method. The samples were prepared in evacuated ampoulas, in order to ensure the oxygen stoichiometry : an uptake of excess oxygen could lead to the appearance of Mn^{4+} and thus to interfering double exchange interactions. It is to be noted that our results on stoichiometric samples differ in some respects from the earlier published data [12,13].

2. Experimental

Samples of $LaMn_{1-x}Ga_xO_3$ (x = 0, 0.15, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1) were prepared by solid state reaction at high temperature (1250°C during 48 h). The reactants (La_2O_3, Mn_2O_3 and Ga_2O_3) were pressed into bars after a thorough mixing, put into small alumina crucibles and sealed into evacuated silica tubes in order to preserve the "O_3" stoichiometry. Chemical titrations of the manganese oxidation state confirmed this O_3 stoichiometry within experimental error.

Numerous crystallites of the compound $LaMn_{0.5}Ga_{0.5}O_3$ were characterized by electron diffraction (ED) and Energy Dispersive Spectroscopy (EDS). The sample was prepared by crushing the grains in alcohol. The small flakes were deposited on a holey carbon film, supported by a copper grid. The reconstruction of the reciprocal space was carried out by tilting around the crystallographic axes with a JEOL 200CX electron microscope.

X-ray powder diffraction patterns were collected at room temperature for 2θ between 15° and 80° in steps of 0.02° on a Philips diffractometer (Cu K_α radiations). Rietveld refinement of the diffractograms was carried out in the Pnma space group with the Fullprof software.

DC magnetic measurements were performed with a Quantum Design SQUID. High temperature susceptibility measurements (T<800 K) were made on a Faraday balance with an applied field of 0.3 T.

3. Results

The thorough EDS analysis of the $LaMn_{0.5}Ga_{0.5}O_3$ sample evidences the good homogeneity of our samples : the actual composition fits with the nominal one, the maximum deviation being 0.02 on each of the cations. The reconstruction of the reciprocal space showed an orthorhombic cell, with $a = a_p\sqrt{2}$, $b = 2a_p$ and $c = a_p\sqrt{2}$ (where a_p is the parameter of the ideal perovskite unit cell, close to 3.8 Å). The conditions limiting the reflections are those of the Pnma space group.

All X-ray diffraction patterns could be refined in the Pnma space group. The cell parameters of our $LaMnO_3$ sample (a = 5.717 Å, $b/\sqrt{2}$ = 5.444 Å, c = 5.533 Å) are in agreement with values found in the literature [14,16]. When the gallium content increases, the distortion of the orthorhombic cell decreases : a decreases, $b/\sqrt{2}$ increases and c remains almost constant. For x<0.6, the lattice remains O' type ($b/\sqrt{2} < c$). From x=0.6, the distortion becomes O^* type, with $b/\sqrt{2} \sim c$. Figure 1 displays the orthorhombic strain 2(a-c)/(a+c) as a function of the gallium content x. It confirms that the orthorhombic strain becomes rather small for x>0.5. The cell volume is also shown in figure 1. Logically, it decreases when the high spin Mn^{3+} ions (radius 0.645 Å) are progressively substituted by the smaller Ga^{3+} ions (radius 0.620 Å).

Figure 2 shows the magnetic moment at 5 K under 5.5 T as a function of the gallium content. The magnetic moments are reported in μ_B/Mn, since Ga^{3+} is a d^{10} ion and does not contribute to the magnetic moment. The magnetic moment first increases until x = 0.3, then remains almost constant up to x = 0.8 and finally vanishes in $LaGaO_3$. Between x = 0.3 and 0.8, the magnetic moment has a value slightly smaller than the theoretical 4 μ_B/Mn of a full ferromagnetic alignment of the Mn^{3+} spins.

Figure 3 displays the m(H) curves at 5 K of the $LaMn_{0.75}Ga_{0.25}O_3$ and $LaMn_{0.7}Ga_{0.3}O_3$ samples. The x = 0.25 sample does not reach saturation under 5.5 T and shows a large hysteresis. The x = 0.3 sample has a ferromagnetic-type behaviour and only a small hysteresis.

Figure 4 displays the high temperature susceptibility data for x = 0.25 and 0.3 between 300 K and 800 K, plotted as $1/\chi$ as a function of temperature. A clear transition at about 600 K is observed in the x = 0.25 curve. On the contrary, no transition is observed in the x = 0.3 curve.

4. Discussion

In manganite compounds with perovskite structure, the manganese ion is surrounded by six oxygen ions. This octahedral environment lifts the degeneracy of the d orbitals into three low energy t_{2g} orbitals and two high energy e_g orbitals. In $LaMnO_3$, the MnO_6 octahedra are additionally distorted by the Jahn-Teller effect : Mn^{3+} is a d^4 high spin ion, therefore the system can reduce its energy if the degeneracy of the e_g levels is lifted. This is achieved by decreasing the symmetry of the octahedra : in $LaMnO_3$, the regular MnO_6 octahedra are deformed into elongated octahedra. Below T_{JT} (Jahn-Teller transition temperature), the long and short Mn-O bonds are ordered : this is called a "cooperative Jahn-Teller effect". This structural feature leads to orbital ordering (OO) because the occupied e_g orbitals are along the longest Mn-O bonds.

The magnetic structure of $LaMnO_3$ [15] is the result of the superexchange (SE) interactions between the Mn^{3+} ions in the orbitally ordered manganese-oxygen network. Stoichiometric $LaMnO_3$ has an A-type antiferromagnetic structure below the Neel temperature T_N. The Mn^{3+} spins are ferromagnetically coupled in the *ac* planes (space group Pnma) and those planes are antiferromagnetically coupled along the *b* axis. It is interesting to note that the temperatures of orbital and spin orderings are decoupled since T_{JT} is about 750 K [16] while T_N is only about 140 K [15].

Contrary to Mn^{3+}, Ga^{3+} is not a Jahn-Teller ion, since it has a d^{10} configuration with fully occupied d orbitals. Therefore Ga^{3+} is expected to affect strongly the physical properties of $LaMnO_3$, even if it does not induce double exchange interactions since Ga^{3+} is isovalent to Mn^{3+}.

The signature of the cooperative Jahn-Teller effect is a transition between two paramagnetic states in the inverse magnetic susceptibility vs. temperature curve. Our results (fig.4) show that the cooperative Jahn-Teller effect disappears for a 30 % Ga substitution. Since an isolated GaO_6 octahedron has no tendency to deformation, it could be expected that for some critical gallium content the cooperative ordering of the long and short Mn-O bonds would vanish. However Mn^{3+} remains a JT ion, therefore some local distortion of the MnO_6 octahedra must persist, but either as an incoherent static effect or as a dynamic effect [17]. Nevertheless the disappearance of the cooperative Jahn-Teller effect is a feature of prime importance, since it coincides with a drastic modification of the magnetic properties. For x up to 0.25, the magnetic behaviour of the compounds remains qualitatively similar to that of $LaMnO_3$: no saturation at 5.5 T and large hysteresis in the m(H) curve. However the increase of the magnetic moment at 5.5 T indicates that the ferromagnetic component increases. At x = 0.3, the cooperative JT effect disappears and the compound has a ferromagnetic-like behaviour and a small hysteresis. Given that the antiferromagnetic order is intimately connected to the orbital ordering, it turns out that the disappearance of the cooperative Jahn-Teller effect is coupled to a disappearance of any long range orbital ordering.

The progressive increase of the ferromagnetic component between x = 0 and x = 0.3 was confirmed by studying the influence of the gallium content on the magnetic moment at 5 K and 5.5 T (fig. 2). However, since those results are obtained with an applied field, it is not possible at this stage to determine the exact nature of the zero field state. There may be either a microscopic phase separation between FM and AFM clusters or a field-induced ferromagnetism. Neutron diffraction patterns will be collected in order to solve this question.

From x = 0.3 to 0.8, the magnetic moment in μ_B/Mn has an almost constant value of 3.7 μ_B/Mn, slightly smaller than the 4 μ_B/Mn of a full ferromagnetic alignment of the Mn^{3+} spins. This apparent independance of the magnetic moment on the dilution by non-magnetic Ga^{3+} ions is rather unexpected. Intuitively it seems that the gallium doping should disrupt the long range magnetic ordering. But in a detailed neutron diffraction study Cussen et al. [17] have also found that long range magnetic ordering takes place in $LaMn_{0.5}Ga_{0.5}O_3$. It is possible that a mechanism of magnetic percolation occurs but this point has to be studied with more detail.

Incidentally, it is interesting to note (fig. 1) that the "transition" from a O' to O* orthorhombic cell at x ~ 0.6 is not coupled to a modification of the physical properties. Conversely, the disappearance of the long range Jahn-Teller order at x ~ 0.3 is not characterized by a significant change in the crystallographic parameters.

Before concluding, our results have to be compared to earlier data published by Goodenough and collaborators. Zhou et al. [12] have studied single crystals of $LaMn_{1-x}Ga_xO_3$ with $x \leq 0.5$. A magnetic moment aproaching 4 μ_B/Mn is reached only at x = 0.5. The disappearance of the JT transition also occurs for a higher x. Those differences might be due to the different synthesis methods. It cannot be ruled out (since no EDS analysis is reported) that the floating zone method could lead to a small shift of the cationic composition [18]. Töpfer et al. [13] have studied polycrystalline samples prepared by coprecipitation of La^{3+} and Mn^{2+} in a solution where solid Ga_2O_3 was dispersed. Again, a magnetic moment approaching 4 μ_B/Mn is reached only at x = 0.5. For the higher gallium concentrations, an almost constant value is observed, as in our samples. Once more, a small compositional shift could be responsible for the difference of results.

5. Conclusions

The substitution of Ga^{3+} on the manganese site of stoichiometric $LaMnO_3$ has a pronounced influence on the physical properties. The cooperative Jahn-Teller effect that leads to orbital and spin orderings in $LaMnO_3$ is perturbed when a spherical d^{10} ion is substituted on the manganese site. The antiferromagnetic structure is progressively destroyed while the ferromagnetic component becomes larger. At x = 0.3, the high temperature JT transition disappears and the compound turns to a typical ferromagnetic material with only small hysteresis. The saturation value is close to the theoretical value for a full alignment of the Mn^{3+} spins. Strangely enough, this value remains almost constant up to 80 % of Ga doping : it seems that the dilution by the non-magnetic Ga^{3+} ion has little effect on the saturation of the Mn spins.

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7. References

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Fig. 1 :
Orthorhombic strain 2(a-c)/(a+c) (left y axis) and cell volume (right y axis) as a function of the gallium content (x)

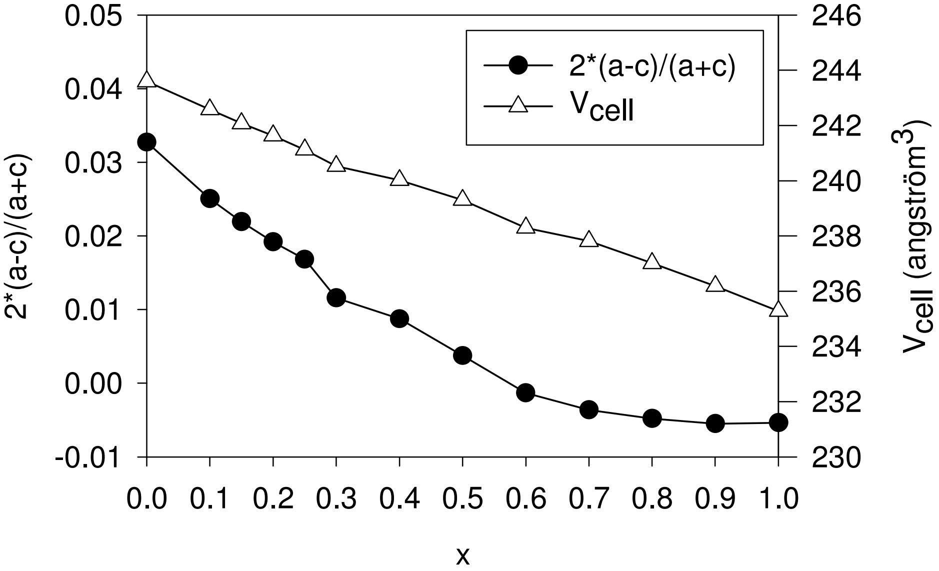

Fig. 2 :
Magnetic moment (in μ_B/Mn) at 5 K and 5.5 T as a function of the gallium content (x)

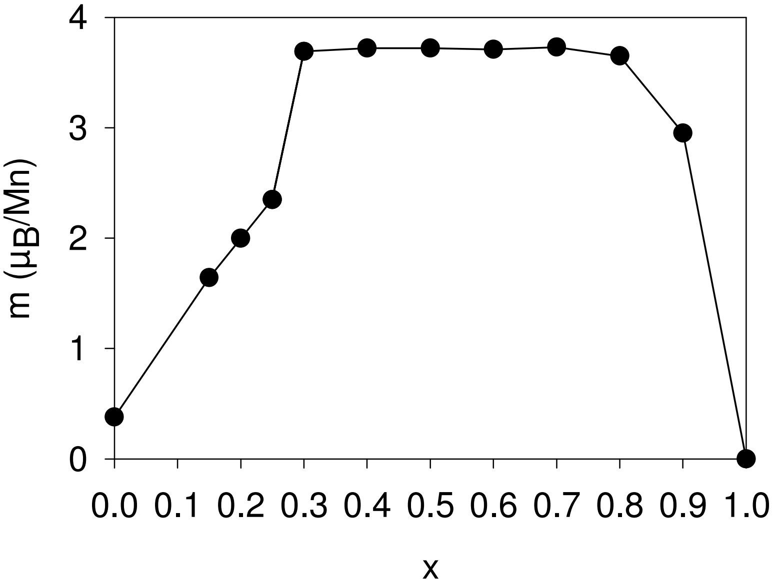

Fig. 3 :
Field dependences of the magnetic moment (in μ_B/Mn) at 5 K for the $LaMn_{0.75}Ga_{0.25}O_3$ and $LaMn_{0.7}Ga_{0.3}O_3$ samples

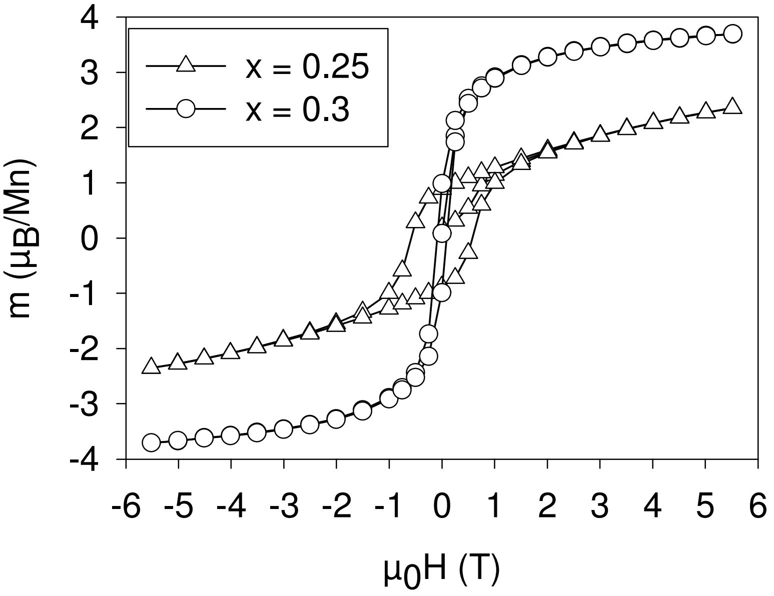

Fig. 4 :
Temperature dependences of the inverse of the high temperature magnetic susceptibility for the $LaMn_{0.75}Ga_{0.25}O_3$ and $LaMn_{0.7}Ga_{0.3}O_3$ samples