# Effect of band filling and structural distortions on the Curie temperature of Fe-Mo double perovskites

Carlos Frontera, Diego Rubi, José Navarro, José Luis García-Muñoz, and Josep Fontcuberta

*Institut de Ciència de Materials de Barcelona, CSIC, Campus Universitari de Bellaterra, E-08193 Bellaterra, Spain*

Clemens Ritter

*Institut Laue Langevin, 6, rue Jules Horowitz, F-38042 Grenoble Cedex 9, France*

By means of high resolution neutron powder diffraction at low temperature we have characterized the structural details of $La_xSr_{2-x}FeMoO_6$ ($0 \leq x \leq 0.5$) and $Ca_xSr_{2-x}FeMoO_6$ ($0 \leq x \leq 0.6$) series of compounds. This study reveals a similar variation of the mean bond-angle $\langle \theta_{\text{Fe-O-Mo}} \rangle$ in both series. In contrast, the mean bond-distance $\langle d_{\text{(Fe,Mo)-O}} \rangle$ increases with La but not with Ca substitution. Both series also present a different evolution of the Curie temperature ($T_C$), which raises in the La series and slightly decreases in the Ca one. We thus conclude that the enhancement of $T_C$ in the La series is due to the electron filling of the conduction band and a concomitant rising of the density of states at the Fermi level.

Double perovskites of the type $A_2FeMoO_6$ ($A =$ Sr, Ba, Ca), have been predicted to be half-metallic ferromagnets up to their Curie temperature ($T_C$), well above room temperature.[1] This fact makes them very attractive from the point of view of applications in magnetoelectronics, and have lead to a growing interest in this and other families of double perovskites. In the ideal double perovskite structure Fe and Mo ions are perfectly ordered in the $B$ position of the perovskite forming two interpenetrating cubic sublattices but, experimentally, this order is not perfect.[2] The low field magnetoresistance is substantial although it decreases as the temperature approaches $T_C$, so in order to enlarge the working range of the potential applications, the main goal of numerous studies has been to enhance the Curie temperature of these compounds. In the celebrated manganites, this objective was achieved by broadening the conduction band, that is, by enlarging the Mn-O-Mn bond angle via the appropriate introduction of large cations in the $A$-site position of the perovskite building block. Using this approach, an enhancement of $T_C$ of about 100 K has been obtained when substituting Ca by Sr in $La_{2/3}Ca_{1/3-x}Sr_xMnO_3$. Interestingly enough, when the same strategy is used in the double perovskites, a very modest enhancement of $T_C$ of only 20 K has been obtained. Indeed, the Curie temperatures of $Ca_2FeMoO_6$ and $Sr_2FeMoO_6$ are of about 380 K (Ref. 3) and 400 K (Refs. 1,2) respectively.

This streaking dissimilarity suggests substantial differences in the nature of the ferromagnetic (FM) coupling in these oxides and suggests that the origin of ferromagnetism (or ferrimagnetism) in double perovskites is different from the double exchange mechanism governing FM manganites.[4] It has been recently proposed that delocalized electrons, antiferromagnetically coupled to localized magnetic moments ($Fe^{3+}:3d^5$), mediate the magnetic coupling, resulting in a net FM interaction between Fe ions. In fact, the magnetic properties, at high temperature (above $T_C$), of $Sr_2FeMoO_6$ can only be properly described if the contribution from delocalized electrons of the conduction band and its antiferro-

magnetic (AFM) interaction with localized spins are taken into account.[5] A direct consequence of this model is that the strength of the FM interaction is governed by (i) the strength of the AFM coupling between core spins and itinerant electrons and (ii) the density of electrons at the Fermi level $[D(E_F)]$. This in turn indicates that a possible way to modify and eventually enhance $T_C$, could be the filling of the conduction band with doping electron carriers. This approach has been proven to be successful and recently a substantial enhancement of $T_C$ by more than 80 K has been reported in $Sr_{2-x}La_xFeMoO_6$ and $(Ba_{0.8}Sr_{0.2})_{2-x}La_xFeMoO_6$ series, where a divalent Sr ion is substituted by a trivalent La ion.[7,8,6] Spectroscopic photoemission measurements have been used to show that indeed $D(E_F)$ in $Sr_{2-x}La_xFeMoO_6$ enhances when $x$ is augmented.[9] Although these experiments did provide a solid confirmation of the relevant role of the itinerant carriers in the FM coupling in double perovskites, they have not settled the microscopic origin of the observed rising of $D(E_F)$. The difficulty arises because in these doped materials, the La substitution not only may provide carriers to the conduction band but also shall promote a structural distortion owing to the different ionic radii of $Sr^{2+}$ and $La^{3+}$ ions. As a result of it, the observed enhancement of $D(E_F)$ cannot be exclusively attributed to a band-filling effect. In sharp contrast with experiments, theoretical analyses, assuming undistorted lattice, have predicted that $T_C$ may lower upon electron doping, in contrast with experiments.[10] Therefore, discrimination between these effects (steric and band filling) is a critical issue for understanding the mechanism of FM coupling in double perovskites and for the design of semimetallic materials having still higher $T_C$.

In order to solve this problem and to elucidate the origin of the $T_C$ enhancement we report here a detailed structural analysis of two complementary series of materials: La substituted and Ca substituted $Sr_2FeMoO_6$. We show that this selection of materials allows one to discriminate between band filling and structural distortion effects. From the com-

TABLE I. Cell parameters and selected bond distances and bond angles of $La_{x_{La}}Sr_{2-x_{La}}FeMoO_6$ and $Ca_{x_{Ca}}Sr_{2-x_{Ca}}FeMoO_6$ found by high-resolution NPD data at $T=10$ K. The reported AS concentration has been obtained by the refinement of XRPD data at RT. $\langle d_{Fe\text{-}O}\rangle$ and $\langle d_{Mo\text{-}O}\rangle$ have been corrected by the presence of antisites. Due to the high concentration of AS in $x_{La}=0.5$ this correction is not realistic and only $\langle d_{(Fe,Mo)\text{-}O}\rangle$ is included. The agreement factors of the NPD data refinement are also reported.

| | $La_{x_{La}}Sr_{2-x_{La}}FeMoO_6$ | | | | $Ca_{x_{Ca}}Sr_{2-x_{Ca}}FeMoO_6$ | | |
|---|---|---|---|---|---|---|---|
| $x_{La}/x_{Ca}$ | 0 | 0.3 | 0.4 | 0.5 | 0.2 | 0.4 | 0.6 |
| SG | $I\,4/m$ | | $P\,2_1/n$ | | | $P\,2_1/n$ | |
| $a$(Å) | 5.5549(1) | 5.5903(2) | 5.5916(2) | 5.5887(2) | 5.5639(2) | 5.5453(2) | 5.5331(3) |
| $b$(Å) | | 5.5655(2) | 5.5656(3) | 5.5642(3) | 5.5511(2) | 5.5386(3) | 5.5328(3) |
| $c$(Å) | 7.9034(2) | 7.8622(3) | 7.8684(3) | 7.8680(3) | 7.8484(3) | 7.8336(3) | 7.8249(3) |
| $\beta$(deg.) | | 89.95(2) | 89.92(2) | 89.90(2) | 90.00(2) | 90.00(2) | 89.99(2) |
| AS (%) | 10 | 25 | 26 | 40 | 5 | 5 | 6 |
| $\langle d_{Fe\text{-}O}\rangle$ | 2.011(4) | 2.008(5) | 2.012(5) | | 2.006(3) | 1.996(3) | 1.993(3) |
| $\langle d_{Mo\text{-}O}\rangle$ | 1.936(4) | 1.955(5) | 1.953(5) | | 1.945(3) | 1.955(3) | 1.957(3) |
| $\langle d_{(Fe,Mo)\text{-}O}\rangle$ | 1.974(2) | 1.982(2) | 1.982(2) | 1.984(3) | 1.975(2) | 1.976(2) | 1.975(2) |
| $\langle \theta_{Fe\text{-}O\text{-}Mo}\rangle$ | 172.6(3) | 167.9(4) | 167.6(4) | 166.3(4) | 167.6(4) | 165.3(5) | 163.2(6) |
| $\chi^2$(%) | 2.4 | 3.9 | 2.1 | 2.9 | 1.9 | 2.2 | 2.8 |
| $R_B$(%) | 4.1 | 4.4 | 4.6 | 4.7 | 3.4 | 3.6 | 3.9 |

parison of the structural and magnetic data we conclusively show that band filling effects dominate and are the responsible of the enhancement of the Curie temperature in La substituted compounds. In contrast, the structural distortions found in the Ca case (similar to those found in the La case) reduce $T_C$.

Ceramic samples of $La_{x_{La}}Sr_{2-x_{La}}FeMoO_6$ ($0 \leqslant x_{La} \leqslant 0.5$) and $Ca_{x_{Ca}}Sr_{2-x_{Ca}}FeMoO_6$ ($0 \leqslant x_{Ca} \leqslant 0.6$) have been synthesized by solid reaction in adequate atmosphere. Stoichiometric amounts of high purity ($>99.99\%$) $Fe_2O_3$, $MoO_3$, $SrCO_3$, $CaCO_3$, and $La_2O_3$ have been mixed. After the initial prefiring treatments to decarbonate the compounds the powders have been pressed into rods. The final firing has been done at $1250\,°C$ in Ar/H-1% (followed by slow cooling down). The quality of the compounds was initially checked by laboratory x-ray powder diffraction (XRPD), using long collecting times in order to obtain very good statistics. The obtained samples are well crystallized and single phased. Only small traces ($\leqslant 0.8\%$) of $SrMoO_4$ have been detected in some patterns. XRPD data have been used to determine the concentration of antisites (AS), defined as the fraction of Fe (Mo) ions in the Mo (Fe) sublattice (thus AS= 50% means full disorder; see Table I).

The neutron powder diffraction (NPD) study has been done at Institut Laue Langevin (Grenoble, France). High-resolution NPD patterns have been collected at the D2B diffractometer (in its high flux mode with $\lambda = 1.594$ Å) at $T = 10$ K using the standard orange cryostat. Samples were kept at this temperature for 15 minutes before data collection. Medium-resolution NPD patterns have been collected at D20 ($\lambda = 2.42$ Å) diffractometer in the range $150$ K$\leqslant T \leqslant 510$ K. High-resolution NPD and XRPD data have been analyzed by the Rietveld method using FULLPROF program.[11]

In agreement with previous studies, we have found that $Sr_2FeMoO_6$ NPD pattern can be very well refined with the tetragonal $I\,4/m$ space group (SG).[12] NPD data reveals that

the substitution with La or Ca induces a structural transition. In La substituted samples an orthorhombic splitting of some peaks and the loose of the $I$-centering displayed by $Sr_2FeMoO_6$ become evident.[7] A change from $I\,4/m$ SG (for $Sr_2FeMoO_6$) to $P\,2_1/n$ SG for $x_{La} \geqslant 0.3$ and $x_{Ca} \geqslant 0.2$ takes place. In Glazer's notation, this corresponds to a change from $a^0a^0c^-$ ($I\,4/m$) to $a^+b^-b^-$ ($P\,2_1/n$) tilt system.[13] This can be attributed to the small size of $La^{3+}$ and $Ca^{2+}$ ions (when compared to that of $Sr^{2+}$ ions), which reduces the tolerance factor of the perovskite structure, thus inducing the rotation of $FeO_6$ and $MoO_6$ octahedra. Most relevant structural details obtained by NPD at 10 K are reported in Table I. The concentration of AS, determined from XRPD, is also given. In all the cases we have checked that the composition is, within the experimental error, the nominal one. In particular, no appreciable deviations from the nominal oxygen content have been found. We have also analyzed the magnetic contribution to the patterns. The large range in $Q$ ($0.4$ Å$^{-1} \leqslant Q \leqslant 7.8$ Å$^{-1}$) of D2B data allows to resolve magnetic and structural parameters without correlations between them. In agreement with previous studies, data in Table I indicates that Ca and La doping promotes[7] and removes[14] respectively the degree of Fe/Mo order.

Data in Table I reveal a systematic enlargement of the average Mo-O bond distance ($\langle d_{Mo\text{-}O}\rangle$) and a shrink of the average Fe-O bond distance ($\langle d_{Fe\text{-}O}\rangle$) in the Ca substituted series. Interestingly enough, the different sign of these evolutions almost compensates and the mean (Fe,Mo)-O bond distance ($\langle d_{(Fe,Mo)\text{-}O}\rangle$) remains nearly constant with $x_{Ca}$. In the La substituted series there is also an enlargement of $\langle d_{Mo\text{-}O}\rangle$ but $\langle d_{Fe\text{-}O}\rangle$ remains nearly constant. This leads to an enhancement of the average octahedral size $\langle d_{(Fe,Mo)\text{-}O}\rangle$ that contrasts with the Ca case as illustrated in Fig. 1(a). On the other hand, in both cases there is a clear bending of the mean Fe-O-Mo bond angle ($\langle \theta_{Fe\text{-}O\text{-}Mo}\rangle$) with substitution [see Fig. 1(b)]. This is due to the rotation of $MO_6$ octahedra caused by
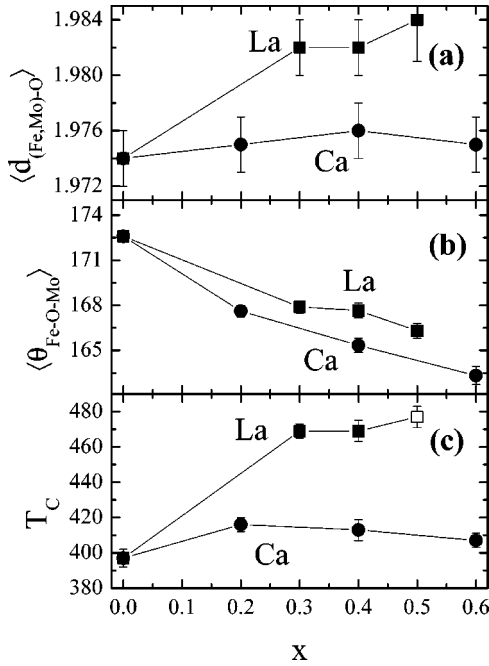
FIG. 1. $\langle d_{\text{(Fe,Mo)-O}} \rangle$ bond distances (a) and $\langle \theta_{\text{Fe-O-Mo}} \rangle$ bond angle (b) found for $\text{La}_x\text{Sr}_{2-x}\text{FeMoO}_6$ and $\text{Ca}_x\text{Sr}_{2-x}\text{FeMoO}_6$ at $T = 10$ K. Solid symbols in (c) show the $T_C$ found from data on Fig. 2; for $x_{\text{La}} = 0.5$ (open square) $T_C$ has been estimated as explained in the text. In all panels squares correspond La and circles to Ca series.
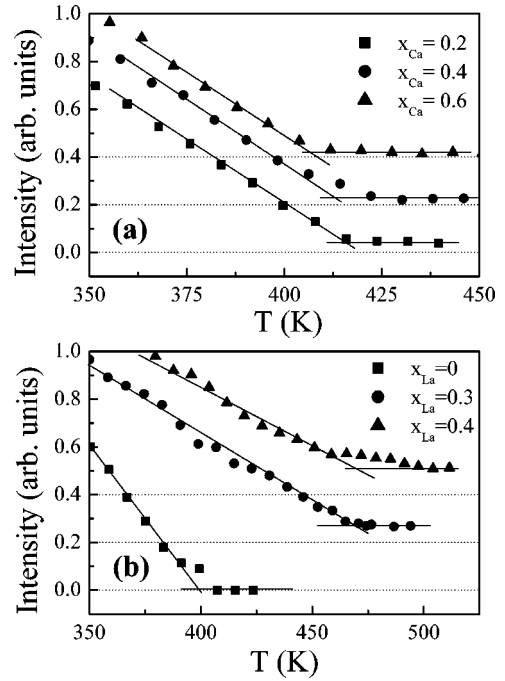


FIG. 2. Integrated intensity of (1 0 1)-(0 1 1) doublet obtained from D20 data for (a) Ca and (b) La substituted compounds. The straight solid lines below $T_C$ are a linear fit to that region and solid lines above $T_C$ correspond to the average value of the intensity. Curie temperatures have been estimated from the crossing point of the straight lines. The curves have been shifted up for clarifying the picture. The dotted lines indicate the zero for, from bottom to top, $x_{\text{Ca}} = 0.2, 0.4,$ and 0.6 (top panel), and $x_{\text{La}} = 0, 0.3,$ and 0.4 (bottom panel).

the smaller size of the $\text{La}^{3+}$ and $\text{Ca}^{2+}$ ions when compared to $\text{Sr}^{2+}$. The smaller size of $\text{Ca}^{2+}$, when compared to that of $\text{La}^{3+}$, explains the stronger bond-bending in Ca series (for the same substitution level).

Figure 2 shows the integrated intensity of the (1 0 1)-(0 1 1) doublet (measured at D20) as a function of temperature for both La and Ca substituted compounds. These reflections are basically of magnetic origin (although a small structural contribution exists in both $I\,4/m$ and $P\,2_1/n$ SG) and thus they can be used to trace the variation of the Curie temperature upon substitution. $T_C$ is clearly indicated by a kink in the temperature dependence of the integrated intensity. The remaining intensity above $T_C$ in the La case can be mainly attributed to the presence of AS and the resulting AFM order above $T_C$.[12] Figure 1(c) collects the values of the Curie temperatures estimated from data in Fig. 2. As already noticed in Ref. 12, the AFM coupling between nearest-neighbor Fe-Fe pairs occurring in the presence of AS, produces an additional magnetic contribution to the (1 0 1)-(0 1 1) doublet above $T_C$ that masks the FM onset in NPD data; indeed the $x_{\text{La}} = 0.5$ sample has AS$\approx 40\%$ and the determination of $T_C$ by NPD data is not accurate. An enhancement of $T_C$ of about 8 K with respect to $x_{\text{La}} = 0.4$ compound was reported from magnetization measurements.[7] Consequently, for $x_{\text{La}} = 0.5$ we have estimated $T_C \approx 477(6)$ K [open square in Fig. 1(c)]. We note in Fig. 1(c) that Ca substitution promotes a very moderated variation of $T_C$: It rises slightly from $x = 0$ to $x_{\text{Ca}} = 0.2$ and lowers gradually for $x_{\text{Ca}} > 0.2$. In contrast, there is an evident growth of $T_C$ from $\text{Sr}_2\text{FeMoO}_6$ to $\text{La}_{x_{\text{La}}}\text{Sr}_{2-x_{\text{La}}}\text{FeMoO}_6$ ($x_{\text{La}} = 0.3, 0.4,$ and 0.5).

We turn now to the comparison of the variation of structural parameters and $T_C$ for both series. In the case of the isoelectronically substituted Ca series, it is clear from Figs. 1(a) and (b) that with a monotonic bending of the $\langle \theta_{\text{Fe-O-Mo}} \rangle$ bond angle while keeping the $\langle d_{\text{(Fe,Mo)-O}} \rangle$ bond-distance constant, a decrease of $T_C$ is found. Therefore closing the $\langle \theta_{\text{Fe-O-Mo}} \rangle$ bond-angle in $A_2\text{FeMoO}_6$ leads to a weakening of the FM coupling and thus to a reduction of $T_C$. The initial increase in $T_C$ ($x_{\text{Ca}} \leq 0.2$) can be attributed to the reduction of AS observed in the Ca-substituted samples (see Table I). In contrast, the La series shows a radically different behavior. With similar values of the bond-bending, $T_C$ raises as much as 80 K. Hence, it follows that the main difference between the structural evolution of both series that can account for the rising of $T_C$ is the expansion of the $\langle d_{\text{(Fe,Mo)-O}} \rangle$ bond in the La case. The enhancement of the $\langle d_{\text{(Fe,Mo)-O}} \rangle$ bond distance indicates that the substitution of divalent $\text{Sr}^{2+}$ by trivalent $\text{La}^{3+}$ leads to the augmentation of the number of electrons within the metallic sublattice of the double perovskite. Taking into consideration that the available electronic states in both Fe and Mo ions are the $t_{2g}$ states that participate in the conduction band,[1] we can asses that the filling of this band is effectively enhanced with La doping.

Aforementioned spectroscopic measurements on $\text{La}_x\text{Sr}_{2-x}\text{FeMoO}_6$ provide evidences that Mo-band states at the Fermi level become gradually filled upon electron-

doping.[9] Data in Table I, is consistent with this finding: $\langle d_{\text{Fe-O}} \rangle$ is nearly constant whereas there is a moderated enhancement of $\langle d_{\text{Mo-O}} \rangle$ ($\Delta \langle d_{\text{Mo-O}} \rangle \approx 0.02$ Å) upon La doping. In agreement with Shannon[15] this small variation of $\langle d_{\text{Mo-O}} \rangle$ bond length would indicate a predominant electron injection at Mo sites.

It is worth to compare the present behavior with that of well known FM manganites where $T_C$ is governed by the bandwidth and by the strong electron-phonon coupling (due to the Jahn-Teller effect).[16,18,17] Both parameters, in manganites, strongly depend on the size of the $A$ cations and the bending of the Mn-O-Mn bond angle drives a strong reduction of $T_C$.[16] As we have shown here, the dependence of $T_C$ on Fe-O-Mo bond angle in double perovskites is much smaller than in manganites. This fact reflects that the strong electron-phonon coupling present in manganites, is not dominant in the present case.

In conclusion, the main structural difference between the two studied series rely on the evolution of the $\langle d_{\text{(Fe,Mo)-O}} \rangle$ bond distance that is constant in Ca case but it is enhanced in the La case. The $\langle \theta_{\text{Fe-O-Mo}} \rangle$ bond angle varying similarly in both series. This indicates that the structural distortion caused by La doping does not significantly alter the FM coupling in $A_2\text{FeMoO}_6$. The enhancement of the $\langle d_{\text{(Fe,Mo)-O}} \rangle$ bond distance in La series signals an effective electron doping in the Fe-Mo sublattice and thus the filling up of the conducting band. Our data conclusively show that the observed reinforcement of the FM coupling in the $\text{La}_x\text{Sr}_{2-x}\text{FeMoO}_6$ series originates from electron-doping effects rather than from structural ones. These findings opens the possibility to design new strategies for further enhancement of $T_C$ and shall be of relevance for microscopic understanding of ferromagnetism in double perovskites.

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