Double perovskites of the type $A_2\text{FeMoO}_6$ ($A = \text{Sr, Ba, Ca}$), have been predicted to be half-metallic ferromagnets up to their Curie temperature ($T_C$), well above room temperature. 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. 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 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.

PACS numbers: 71.20.Ps, 61.12.Ld, 75.30.Et, 75.47.Gk
TABLE I: Cell parameters and selected bond distances and bond angles of La\textsubscript{1x_{La}}Sr\textsubscript{2-x_{La}}FeMoO\textsubscript{6} and Ca\textsubscript{x_{Ca}}Sr\textsubscript{2-x_{Ca}}FeMoO\textsubscript{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-O} \rangle) and (\langle d_{Mo-O} \rangle) have been corrected by the presence of antisites. Due to the high concentration of AS in x\textsubscript{La} = 0.5 this correction is not realistic and only (\langle d_{(Fe,Mo)-O} \rangle) is included. The agreement factors of the NPD data refinement are also reported.

| x\textsubscript{La}/x\textsubscript{Ca} | 0 | 0.3 | 0.4 | 0.5 | 0.2 | 0.4 | 0.6 |
|---|---|---|---|---|---|---|---|
| SG | I\textsubscript{4}/m | P\textsubscript{2}1/n | P\textsubscript{2}1/n |
| a (Å) | 5.5939(2) | 5.5916(2) | 5.5887(2) | 5.5639(2) | 5.5453(2) | 5.5331(3) |
| b (Å) | 5.5656(2) | 5.5656(3) | 5.5642(3) | 5.5511(2) | 5.5386(3) | 5.5328(3) |
| c (Å) | 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) |
| AS (%) | 10 | 25 | 26 | 40 | 5 | 5 | 6 |
| \(\langle d_{Fe-O} \rangle\) | 2.008(5) | 2.008(5) | — | 2.006(3) | 1.996(3) | 1.993(3) |
| \(\langle d_{Mo-O} \rangle\) | 1.953(5) | 1.953(5) | — | 1.945(3) | 1.955(3) | 1.957(3) |
| \(\langle d_{(Fe,Mo)-O} \rangle\) | 1.982(2) | 1.982(2) | 1.984(3) | 1.975(2) | 1.976(2) | 1.975(2) |
| \(\theta_{Fe-O-Mo}\) | 172.6(3) | 167.9(4) | 167.6(4) | 166.3(4) | 166.7(4) | 165.3(5) |
| \(\chi^{2}\) | 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 |

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\textsubscript{2}FeMoO\textsubscript{6}. We show that this selection of materials allows to discriminate between band-filling and structural distortion effects. From the comparison 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\textsubscript{1x_{La}}Sr\textsubscript{2-x_{La}}FeMoO\textsubscript{6} (0 ≤ x\textsubscript{La} ≤ 0.5) and Ca\textsubscript{x_{Ca}}Sr\textsubscript{2-x_{Ca}}FeMoO\textsubscript{6} (0 ≤ x\textsubscript{Ca} ≤ 0.6) have been synthesized by solid reaction in adequate atmosphere. Stoichiometric amounts of high purity (> 99.99%) Fe\textsubscript{2}O\textsubscript{3}, MoO\textsubscript{3}, SrCO\textsubscript{3}, CaCO\textsubscript{3}, and La\textsubscript{2}O\textsubscript{3} have been mixed. After the initial prefireing 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 (≤ 0.8%) of SrMoO\textsubscript{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 II).

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 ≤ \(T \leq 510\) K. High-resolution NPD and XRPD data have been analyzed by the Rietveld method using FullProf program.

In agreement with previous studies, we have found that Sr\textsubscript{2}FeMoO\textsubscript{6} NPD pattern can be very well refined with the tetragonal I\textsubscript{4}/m space group (SG)\textsuperscript{2,3} 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\textsubscript{2}FeMoO\textsubscript{6} become evident. A change from I\textsubscript{4}/m SG (for Sr\textsubscript{2}FeMoO\textsubscript{6}) to P\textsubscript{2}1/n SG for x\textsubscript{La} ≥ 0.3 and x\textsubscript{Ca} ≥ 0.2 takes place. In Glazer’s notation, this corresponds to a change from a\textsuperscript{0}a\textsuperscript{0}c\textsuperscript{−} (I\textsubscript{4}/m) to a\textsuperscript{0}a\textsuperscript{0}c\textsuperscript{−} (P\textsubscript{2}1/n) tilt system.\textsuperscript{2,3} This can be attributed to the small size of La\textsuperscript{3+} and Ca\textsuperscript{2+} ions (when compared to that of Sr\textsuperscript{2+} ions), which reduces the tolerance factor of the perovskite structure, thus inducing the rotation of FeO\textsubscript{6} and MoO\textsubscript{6} octahedra. Most relevant structural details obtained by NPD at 10 K are reported in Table II. 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 \(Q (0.4\text{Å}^{-1} \leq Q \leq 7.8\text{Å}^{-1})\) of D2B data allows to resolve magnetic and structural parameters without correlations between them. In agreement with previous studies, data in Table II indicates that La and Ca doping promotes and removes respectively the degree of Fe/Mo order.

Data in Table II reveal a systematic enlargement of the average Mo-O bond-distance (\(\langle d_{Mo-O} \rangle\)) and a shrink of the average Fe-O bond-distance (\(\langle d_{Fe-O} \rangle\)) in the Ca sub-
stutted series. Interestingly enough, the different sign of these evolutions almost compensates and the mean (Fe,Mo)-O bond distance ($\langle d_{Fe,Mo-O} \rangle$) remains nearly constant with $x_Ca$. In the La substituted series there is also an enlargement of $\langle d_{Mo-O} \rangle$ but $\langle d_{Fe-O} \rangle$ remains nearly constant. This leads to an enhancement of the average octahedral size ($\langle d_{Fe,Mo-O} \rangle$) 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 ($\langle \theta_{Fe-O-Mo} \rangle$) with substitution [see Fig. 1(b)]. This is due to the rotation of MO$_6^{2+}$ when compared to Sr$^{2+}$ caused by the smaller size of the La$^{3+}$-$O$-Mo bond angle ($\langle \theta_{Fe-O-Mo} \rangle$) with substitution. Consequently, for $x_{La} = 0.5$ 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 $x_Ca = 0.2$ and lowers gradually for $x_Ca > 0.2$. In contrast, there is an evident growth of $T_C$ from Sr$_2$FeMoO$_6$ to La$_{x_{La}}$Sr$_{2-x_{La}}$FeMoO$_6$ ($x_{La} = 0.3, 0.4$ 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 Fig. 1(a) and (b) that with a monotonic bending of the $\langle \theta_{Fe-O-Mo} \rangle$ bond-angle while keeping the $\langle d_{Fe,Mo-O} \rangle$ bond-distance constant, a decrease of $T_C$ is found. Therefore closing the $\langle \theta_{Fe-O-Mo} \rangle$ bond-angle in A$_2$FeMoO$_6$ leads to a weakening of the FM coupling and thus to a reduction of $T_C$. The initial increase in $T_C$ ($x_Ca \leq 0.2$) 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

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{\(\langle d_{Fe,Mo-O} \rangle\) bond-distances (a) and $\langle \theta_{Fe-O-Mo} \rangle$ bond-angle (b) found for La$_{x_{La}}$Sr$_{2-x_{La}}$FeMoO$_6$ and Ca$_{x_{Ca}}$Sr$_{2-x_{Ca}}$FeMoO$_6$ at $T = 10$ K. Solid symbols in (c) show the $T_C$ found from data on Fig. 2 for $x_{La} = 0.5$ (open square) $T_C$ has been estimated as explained in the text. In all panels squares correspond La and circles to Ca series.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2.png}
\caption{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, $x_Ca = 0.2, 0.4$ and $0.6$ (top panel), and $x_{La} = 0.3$ and $0.4$ (bottom panel).}
\end{figure}
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 \( \langle d_{\text{Fe-Mo}-\text{O}} \rangle \) bond in the La-case. The enhancement of the \( \langle d_{\text{Fe-Mo}-\text{O}} \rangle \) bond distance indicates that the substitution of divalent Sr\(^{2+}\) by trivalent 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, we can assess that the filling of this band is effectively enhanced with La doping.

Aforementioned spectroscopic measurements on La\(_{1-x}\)Sr\(_{2}\)FeMoO\(_6\) provide evidences that Mo-band states at the Fermi level become gradually filled upon electron-doping.\(^{22}\) Apparently, data in Table 1 is consistent with this finding: \( \langle d_{\text{Fe}-\text{O}} \rangle \) is nearly constant whereas there is a moderated enhancement of \( \langle d_{\text{Mo}-\text{O}} \rangle \) \( (\Delta \langle d_{\text{Mo}-\text{O}} \rangle \approx 0.02 \text{ Å}) \) upon La-doping. In agreement with Shannon\(^{22}\) this small variation of \( \langle d_{\text{Mo}-\text{O}} \rangle \) 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).\(^{16,17,18}\) 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 \( T_C \).\(^{16,18}\) 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 \( \langle d_{\text{Fe-Mo}-\text{O}} \rangle \) bond distance that is constant in Ca case but it is enhanced in the La case. The \( \langle \theta_{\text{Fe}-\text{O}-\text{Mo}} \rangle \) 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\(_2\)FeMoO\(_6\). The enhancement of the \( \langle d_{\text{Fe-Mo}-\text{O}} \rangle \) 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 La\(_{1-x}\)Sr\(_{2}\)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.

Acknowledgments

We thank the AMORE (EU), MAT 1999-0984-C03 and MAT 2002-03431 (CICYT, spanish government), and 2001SGR-00334 (Generalitat de Catalunya) projects for financial support. C.F. acknowledges financial support from MCyT (Spain). We thank ILL for the provision beam time.