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Raising the Curie temperature in Sr_2FeMoO_6 double perovskites by electron doping

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Electron doping in the ferromagnetic and metallic double perovskites Sr_2FeMoO_6 is achieved via the partial substitution of Sr^{2+} by La^{3+}. We show that this doping promotes an extraordinary rising of the Curie temperature of about 70 K above that of the pristine compound. This finding reveals that the ferromagnetic coupling is mediated by itinerant carriers, thus providing solid experimental support to the double-exchange picture for the magnetic interactions. The observation that T_C can be substantially enhanced may be of relevance for technological applications of these materials in advanced spin devices.

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Carrier doping in strongly correlated electron systems has been a very successful tool to disclose some of the most exciting new phenomena and materials in the last few years. High-T_C superconducting cuprates and the so-called manganese perovskites are among the most celebrated examples. In this last case, the parent compound $LaMnO_3$ is insulating and antiferromagnetic; by suitable hole doping, such as $La_{1-x}Sr_xMnO_3$, metallic and ferromagnetic behavior is promoted. In ferromagnetic manganese perovskites, the itinerant charge carriers (holes) via the so-called double-exchange (DE) mechanism mediate the ferromagnetic coupling.[1] Within this framework, the strength of the ferromagnetic coupling and, thus, the Curie temperature (T_C) is controlled mainly by the width of the conduction band (W) (Refs. 2 and 3) and the itinerant charge density $n(\approx x)$.[4] In $L_{1-x}A_xMnO_3$ (L is a lanthanide and A is an alkaline-earth ion), the bandwidth W is determined by the bending of the Mn-O-Mn bonding angle, which varies with the ionic radius of the (L,A) ions.[2,3]

Recently, double-perovskite oxides of the type A_2FeMoO_6 ($A=$Ca,Sr,Ba), being also half-metallic ferromagnets,[5] have received a great deal of attention because they display a substantial magnetoresistance and their Curie temperature is well above that of the optimally doped $La_{2/3}Sr_{1/3}MnO_3$ ($T_C\approx 360$ K) simple perovskite. Indeed, Curie temperatures about 400–430 K have been reported for Sr_2FeMoO_6 (Ref. 5) and even higher ($T_C\approx 500$ K) for Sr_2FeReO_6.[6] This fact pushes the operation range for eventual applications well above room temperature.

It has been recently shown that the dominant magnetic interaction in A_2FeMoO_6 double perovskites is ferromagnetic,[7] thus implying that the ferrimagneticlike ordering does not come from a nearest-neighbor antiferromagnetic interaction as commonly found in other oxides (in spinells, for instance). Instead, it signals that the magnetic interactions are not of superexchange origin but more likely of DE type as found in the manganese perovskites. Indeed, the reported correlation between the electrical resistivity and the Curie temperature[8] as well as the correlation discovered between T_C and the Fe-O-Mo bonding angle[9] also points in this direction. Unfortunately, strategies to increase T_C based on size effects (for instance, by substitution of Sr by Ba or Ca) invariably lead to a reduction of T_C.[10]

In this paper we will show that charge doping, i.e., modifications of the density of charge carriers in the conduction band, provides an efficient way to increase the Curie temperature of these metallic oxides. Electron doping is achieved by appropriate substitution of the divalent alkaline earth by a trivalent lanthanide. We will show that $Sr_{2-x}La_xFeMoO_6$ ($0<x<1$) oxides can be prepared with T_C rising from about 400 K for $x\approx 0$ to about $T_C\approx 490$ K for $x\approx 1$.

Ceramic samples have been prepared by solid-state reaction at high temperature. $SrCO_3$, La_2O_3, Fe_2O_3, and MoO_3 oxides have been mixed at stoichiometric ratios appropriate to obtain $Sr_{2-x}La_xFeMoO_6$ ($x=0$–1). In the first step, oxide mixtures are prereacted at 900 °C under air. After grinding, the samples are pelletized and sintered at $T_S=1200\,°C$ under an Ar/H_2 (5%) atmosphere for 12 h. The process is repeated several times in order to complete the reaction. Samples are heated and cooled at a rate of 5 °C/min under the same atmosphere. Results from different batches (B1 and B2) prepared under nominally identical conditions will be presented. Energy-dispersive x-ray analysis and inductively coupled plasma (ICP) methods indicate that the ratio of concentrations of Sr/La/Mo/Fe atomic species in the samples vary according to the expected ratio within the typical experimental accuracy ($<2\%$). Room-temperature x-ray powder diffraction (XRPD) experiments have been performed using a Rigaku Ru-200B diffractometer and k_{α_1,α_2}(Cu) radiation. The obtained profiles have been analyzed using the FULLPROF program.[11] The magnetization and magnetotransport properties has been measured by using a Quantum Design superconducting quantum interference device (SQUID) magnetometer up to 5.5 T and in the 10–700 K temperature range. The magnetic- and temperature-dependent resistivity has been measured in a PPMS (Quantum Design).

XRPD patterns of samples with $0\leqslant x<0.4$ can be well refined ($\chi^2=1.8$, $R_{wp}=11.2$–11.1%) using the tetragonal (T) $I4/mmm$ space group (SG). Patterns of samples with $x\geqslant 0.4$ present orthorhombic (O) distortions. For instance, (2 0 2) Bragg reflection of an $x=0.2$ compound [Fig. 1(a)] splits into (2 0 2) and (0 2 2) in an $x=0.6$ compound [Fig. 1(b)]. For $0.4\leqslant x\leqslant 0.8$ successful refinements ($\chi^2=2.0$, $R_{wp}=11.0$–11.6%) can be achieved using the monoclinic

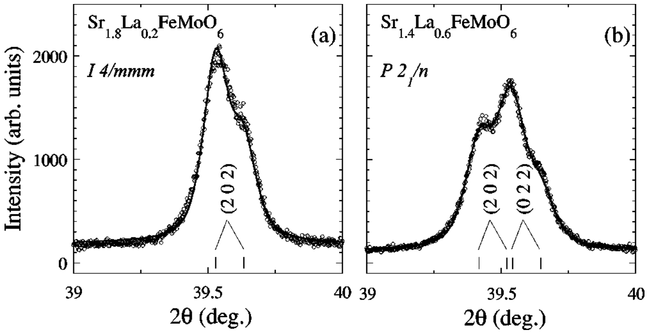

FIG. 1. Detail of the x-ray pattern [using k_{α_1,α_2}(Cu) radiation] of the $Sr_{2-x}La_xFeMoO_6$, $x=0.2$ and $x=0.6$, samples (a) and (b), respectively.

(M) $P\,2_1/n$ SG (although the monoclinic angle β does not significantly differ from 90°). For $x \geqslant 0.8$ the patterns can be successfully refined using either $P\,2_1/n$ or $P\,bnm$ SG (O leading to $\chi^2=1.8$ and $R_{wp}=11.2$–$11.5\,\%$). For $x \geqslant 0.8$ minor traces of impurities (below 2%) could be observed.

Figure 2(a) shows the obtained lattice parameters as a function of the doping level x. Results from a recent paper by Moritomo *et al.*,[12] using synchrotron XRPD in the doping region $0 \leqslant x \leqslant 0.3$, have been also included for completeness. This figure evidences that the onset of the O distortion at $x \approx 0.3$–0.4 is accompanied by sudden structural changes, and that there is a considerable cell expansion upon La substitution. The ionic radius of La^{3+} is smaller than that of the Sr^{2+}; therefore the cell expansion is not motivated by the steric effects associated with the ionic sizes but it reflects electronic effects. Indeed, it signals electron doping into the antibonding orbitals of t_{2g}^* and e_g^* parentage of Fe and Mo ions. This electron doping, which leads to an expansion of the mean radius of the atomic species at (B,B') sites of the $(A_{2-x}A'_x)BB'O_6$ network *and* the reduction of the mean size of the (A,A') cations drive to a reduction of the Goldschmidt tolerance factor t and justify the reduction of symmetry upon doping.[13]

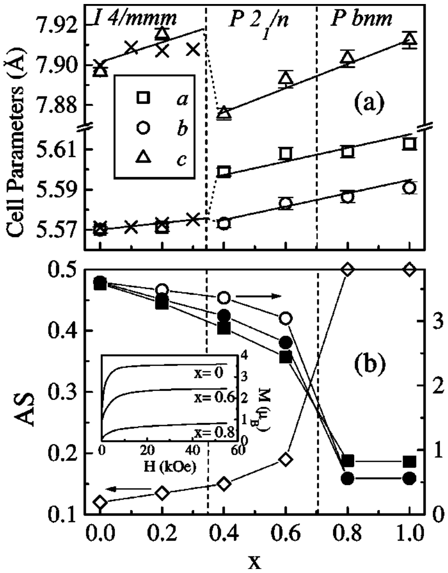

FIG. 2. (a) Cell parameters as a function of La doping (x) in $Sr_{2-x}La_xFeMoO_6$. For $x \leqslant 0.3$, cell parameters from Ref. 12 (×) are also included. (b) Antisite concentration AS (◇, left axis) and saturation magnetization M_S (10 K,5.5 kOe) (■, right axis) of $Sr_{2-x}La_xFeMoO_6$ samples. ● and ○ correspond to the calculated $M_S^C(\mathrm{AS},x)$ values as explained in the text. Inset: field-dependent magnetization measured at 10 K.

From the Rietveld refinement we have also evaluated the mixing of Fe and Mo species in the (B,B') sites, i.e., the antisite (AS) defect concentration.[14] As shown in Fig. 2(b), there is a progressive rising of the antisite defects when increasing x. In fact, for $x > 0.8$ refinements lead to values of the AS disorder of about $\sim 0.50(2)$, thus indicating that, within the sensitivity of the x-ray pattern, no significant ordering of Fe and Mo species within the (B,B') sublattices of $P\,2_1/n$ SG exists. Consequently, for $x > 0.8$ a description using the $P\,bnm$ space group, where only one single Wyckoff position for Fe/Mo ions exists, is preferred. The reduction of the Fe/Mo ionic ordering upon La substitution indicates that there is a charge transfer towards the (B,B') sites in such a way that the charge difference among Fe^{m+} and $Mo^{m'+}$ species is reduced.[13] The spin-down subbands of $4d$(Mo), crossing the Fermi level,[5] likely become partially filled with doping electrons.[12]

We turn now to the field dependence of the magnetization $M(H,x)$. The magnetization curves measured at 10 K [see inset in Fig. 2(b)] indicate that all samples are ferromagnetic. The technical saturation is reached at fields below 10 kOe. However, there is a remarkable reduction of the saturation magnetization (M_S) when raising the La content. This can be appreciated in Fig. 2(b) (right axis) where the M_S (10 K, 55 kOe) values are included. Interestingly enough, we note that the $M_S(x)$ dependence essentially mimics that of the order parameters AS(x), thus suggesting that the saturation magnetization is progressively reduced by antisite defects. In fact, similar behavior has been well documented in the undoped Sr_2FeMoO_6 oxides.[14,15] It should be noted, however, that electron doping at the (B,B') spin-down subbands[5] should also produce an additional reduction of the saturation magnetic moment.

In order to settle if the AS disorder is the main reason for the progressive reduction of M_S we have calculated $M_S(x)$ assuming (a) an antiparallel spin alignment between the B and B' sublattices and (b) that La doping promotes a progressive electron doping at the (B,B') sublattice. Under these circumstances M_S can be written as

$$M_S^C(\mathrm{AS},x)=(1-2\mathrm{AS})[m(\mathrm{Fe})-m(\mathrm{Mo})]+(1-2\mathrm{AS})\times[\Delta m(\mathrm{Fe})-\Delta m(\mathrm{Mo})], \qquad (1)$$

where m(Fe) and m(Mo) are the magnetic moments of Fe^{m+} and $Mo^{m'+}$ ions and Δm(Fe) and Δm(Mo) represent the corresponding change of moment after electron doping. The first term in right member of Eq. (1) represents the contribution of the antisite disorder to M_S. The corresponding $M_S^C(\mathrm{AS},0)=4(1-2\mathrm{AS})\mu_B$ values[14] are plotted in Fig. 2(b) as open circles. The second term collects the reduction of moment associated with the electron doping. Assuming that

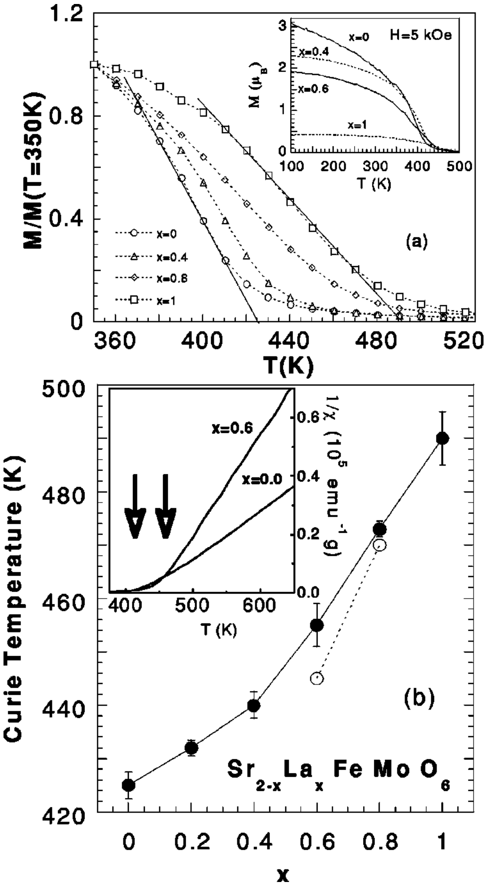

FIG. 3. (a) Main panel: reduced magnetization $M(T,5\ \mathrm{kOe})/M(350\ \mathrm{K},5\ \mathrm{kOe})$ vs temperature for $\mathrm{Sr}_{2-x}\mathrm{La}_x\mathrm{FeMoO}_6$ ($x=0$, 0.4, 0.8, and 1) samples. Inset: temperature-dependent magnetization. (b) Dependence of the Curie temperature on the La doping (x) in $\mathrm{Sr}_{2-x}\mathrm{La}_x\mathrm{FeMoO}_6$. Solid and open circles correspond to samples from different batches. Inset: high-temperature inverse paramagnetic susceptibility ($H=5$ kOe) of $x=0$, 0.6 and $x=1$ samples. The arrows indicate the extrapolated paramagnetic Curie temperature.

the electronic transfer from the doping specie in the A sites towards the (B,B') sites is complete, it can be written as $x(2\mathrm{AS}-1)\mu_B$. The solid circles in Fig. 2(b) represents the total calculated $M_S^C(\mathrm{AS},x)$. In Fig. 2(b), all $M_S^C(\mathrm{AS},x)$ have been shifted by constant amount in such a way that $M_S^C(\mathrm{AS},0)$ coincides with the experimental value. Figure 2(b) shows that although the sharp drop in M_S upon La doping is mainly controlled by a loosening of the Fe/Mo ordering, particularly at the $T\Rightarrow O$ transition, there is a clear contribution (the difference between the solid and open circles) of the electronic transfer which further reduces M_S.

The temperature dependence of the magnetization (measured at 5 kOe) is shown in Fig. 3(a) (inset). Data in this figure immediately reveal the key result of this paper, that is, the progressive rising of T_C when increasing the La content (x). This can be better appreciated in the main panel of Fig. 3(a) where the normalized magnetization $M(T)/M(350\ \mathrm{K})$ is shown for some samples. The dependence of T_C on the La doping rate is summarized in Fig. 3(b). We must stress that for $x=1$, $T_C\approx 490$ K, i.e., about ~ 70 K above that of the unsubstituted $(x=0)$ sample. To assess the reproducibility of experiments, we also include some data from samples of batch B1.

In a recent paper, Moritomo *et al.*[12] explored the La/Sr substitution only up to $x=0.3$ and failed to observe any significant enhancement of T_C. Consistently, our data of Fig. 2 reveal a modest enhancement of T_C ($\sim 8-10$ K) in this composition range. To what extent this difference arises from a slightly oxygen stoichiometry may be related to the different atmospheres used (Ar in Ref. 12 and Ar/H_2 in the present paper). This remains to be elucidated.

The ferromagnetic nature of the dominant interactions in all samples can be also inferred from the values of the paramagnetic Curie temperature (θ_P) extracted from measurements of the magnetic susceptibility in the paramagnetic phase. In Fig. 3(b) (inset) we show some of the susceptibility data collected at high temperature. It can be appreciated that θ_P are positive, thus indicating ferromagnetic interactions. It is also clear from Fig. 3(b) that θ_P increases upon La substitution, thus revealing that the ferromagnetic interactions are reinforced when increasing the electron doping. Consistently with the M_S data of Fig. 2(b), the effective moment μ_{eff} decreases when raising x. We shall note that the observation of a dominant ferromagnetic interaction rules out the ferrimagnetic model commonly used to rationalize the magnetic structure of these oxides and provides strong support to the double-exchange coupling mechanism.[7]

Within the DE scenario, the extraordinary rising of T_C upon La doping can be understood as a direct consequence of the increasing carrier density. Indeed, the structural and magnetization data strongly signal a progressive charge filling of the (B,B') spin-down subbands. Upon La substitution, the Fe-O-Mo bonds are progressively closed as indicated by the tendency towards an orthorhombic symmetry. In this case, the hopping integral Fe-O-Mo of e_g parentage should be reduced. In the manganese perovskites, where the conduction band is primarily of e_g parentage, this results in a reduction of the effective bandwidth (W) and thus of T_C. In the double perovskites, however, the conduction band is mainly formed by $\mathrm{Mo}(t_{2g})$ orbitals, pointing along the diagonals of the perovskite, and thus there is a direct $\mathrm{Mo}(t_{2g})$-$\mathrm{Mo}(t_{2g})$ interaction. When upon doping, the cell distorts and expands, and likely the hopping integral $t(t_{2g})$ also weakens and thus W narrows. Consequently, steric effects should also reduce W and so lower T_C: thus they cannot account for the experimental data. We thus conclude that the rise of T_C is primarily driven by an electronic effect. It has been recently predicted that electron doping may indeed promote some modification of T_C in these oxides.[16]

Upon La doping the electrical resistivity of the samples does not change significantly: for instance, $\rho(300\ \mathrm{K},x=0)\approx\rho(300\ \mathrm{K},x=0.8)\approx 1\ \Omega\,\mathrm{cm}$. This suggests that in these ceramic samples, intergranular effects mainly control the measured resistivity and thus the intrinsic metallic nature of the undoped material likely is preserved.[2,5,17] Of a major concern for eventual technological applications is the magnetoresistance of the doped samples. In Fig. 4 we show, as an example, the field-dependent resistance $R(H)/R(H=0)$ of the $x=0$ and 0.8 samples at $T=10$ K and 300 K. It is clear

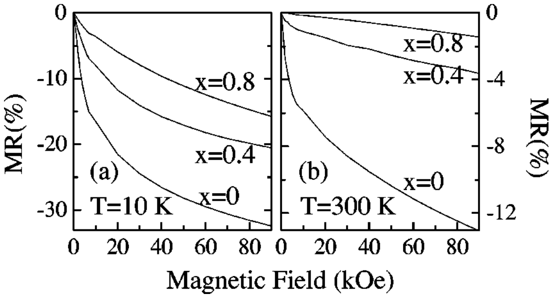

FIG. 4. Field dependence of the resistance $R(H)/R(H=0)$ at (a) 10 K and (b) 300 K of the $\mathrm{Sr}_{2-x}\mathrm{La}_x\mathrm{FeMoO}_6$, $x=0$, 0.4, and 0.8 samples.

from this figure that, in spite of the reduced magnetization of the $x=0.8$ sample when compared to the $x=0$ one, the magnetoresistance $R(90\ \mathrm{kOe})/R(H=0)$ at 10 K is about $\approx 18\%$, which is comparable to the values reported for undoped $(x=0)$ materials.[5,17]

In summary we have shown that by appropriate electron doping, the T_C of $A_{2-x}A'_xBB'\mathrm{O}_6$ double perovskites can be raised well above $(\Delta T_C \approx 70\ \mathrm{K})$ that of the undoped materials. Both low-temperature magnetization loops and the values of the paramagnetic Curie temperature indicate that the samples are ferromagnetic and that the ferromagnetic interactions are reinforced upon doping. A substantial reduction of the saturation magnetization is observed. We have shown that it partially originates from the electron doping of the (B,B') network, but it mainly results from the presence of antisite disorder. We have found that this becomes prominent in the O phases obtained at high doping levels. We thus may suggest that cationic substitutions in the (A,A') sublattice leading to a higher tolerance factor could lead to materials in which the $T \Rightarrow O$ transition is suppressed and appropriate metallurgical treatments may improve the (B,B') ordering and thus the overall magnetization of the samples. The present results can be understood within the framework of a double-exchange-mediated ferromagnetic interactions and illustrate a method of tailoring the magnetotransport properties of half-metallic ferromagnetic double perovskites.

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