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Increase of Curie temperature in fixed ionic radius $Ba_{1+x}Sr_{1-3x}La_{2x}FeMoO_6$ double perovskites

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Abstract. We study the influence of electron doping in $Ba_{1+x}Sr_{1-3x}La_{2x}FeMoO_6$ ($x \leq 0.3$) double perovskites, where the designed combination for the cationic site minimizes the influence of steric effects. We find an increase of the Curie temperature (T_C), which supports the claim of the important role played by the band filling in the value of T_C. Other effects like changes in the bare electronic bandwidth (determined by structural parameters) and Fe/Mo antisite defects seem to play a less relevant role in the increase of T_C in this series. Changes in structural parameters, magnetization and magnetotransport properties as a function of Ba/La doping are correlated with an increase of the density of states at the Fermi level and a moderate rise of antisites.

PACS. 75.30.Kz Magnetic phase boundaries (including magnetic transitions, metamagnetism, etc.) – 75.30.Cr Saturation moments and magnetic susceptibilities – 72.25.Mk Spin transport through interfaces – 61.12.Ld Neutron diffraction – 75.70.Pa Giant magnetoresistance – 75.50.Gg Ferrimagnetics

1 Introduction

Some ordered double perovskites $A_2BB'O_6$ (A = Ca, Sr, Ba, La, etc.; BB' = FeMo, FeRe, CrRe, etc.) are magnetic oxides which show relevant properties in the field of Spin Electronics. Properties like half metallicity [1] and high Curie temperature, T_C, (up to 635 K [2]) make these compounds attractive for their implementation in magnetic tunnel junctions [3], low-field magnetoresistive sensors [4], etc.

A detailed structural and magnetic study in $AA'FeMoO_6$ suggested that at fixed electronic conduction band filling, T_C is controlled by the structural parameters that determine the electronic bandwidth [5]. Another way in order to enhance T_C seems to be the increase in the number of conduction electrons as has been realized with La doping at the A site [6,7]. However, in references [6,7], steric effects due to large structural variations occur simultaneously to the change in the band filling and it is difficult to separate both contributions. A recent theoretical study concludes that without the introduction of structural changes, non-stoichiometry, or antisite defects, T_C would decrease with the number of conduction electrons [8]. As a consequence, changes in the crystallographic structure, the electronic bandwidth or a substantial increase of antisites occurring in the series studied in references [6,7] can be responsible for the measured increase in T_C, at least in part.

In order to study experimentally *the influence of the band filling alone*, we have synthesized the series with nominal composition $Ba_{1+x}Sr_{1-3x}La_{2x}FeMoO_6$ (x = 0, 0.1, 0.2 and 0.3; for obvious reasons doping is feasible in this series only up to $x = 0.33$) where the steric effects are minimized and electron doping of the conduction band is achieved. According to reference [9], in the case of coordination number equal to 12 (which is the case with these cubic double perovskites), the ionic radii of Ba^{2+}, Sr^{2+} and La^{3+} are respectively 1.61 Å, 1.44 Å, and 1.36 Å. This means that by replacing Sr ions from the parent compound $BaSrFeMoO_6$ with one third of Ba ions and two thirds of La ions, the nominal ionic radius of the A site does not change. We think that this kind of doping can be an effective way to reduce the steric effects. La doping assures an increase in the number of conduction electrons as explained hereafter. In the parent compound $BaSrFeMoO_6$, the $3d$ spin-up subband is full and there is one electron per Fe/Mo couple in the spin-down subband, which crosses the Fermi level and constitutes the conduction band [1]. As La^{+3} replaces Sr^{+2} ions in $Ba_{1+x}Sr_{1-3x}La_{2x}FeMoO_6$, the number of electrons at the Fermi level will be modified to $(1+2x)$ per formula unit. A similar assumption has been used in $Sr_{2-x}La_xFeMoO_6$ and confirmed by means of photoemission experiments [10].

In the next sections we will report the structural, magnetic and magnetotransport study carried out on this series of compounds by means of X-ray diffraction, neutron diffraction, magnetization, and transport measurements.

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This study allows us to conclude that T_C increases with the band filling. Ba/La doping seems to introduce some structural changes and antisite defects and these changes are used in order to interpret the magnetic and magnetotransport properties. An NMR and XMCD study has also been performed on these samples supporting these conclusions [11].

The samples were prepared by solid state reaction. Stoichiometric amounts of $BaCO_3$, $SrCO_3$, La_2O_3, Fe_2O_3, and MoO_3 were mixed, ground and calcined twice at 900 °C for 2 hours in air. The calcined mixture were reground, pressed and sintered twice at 1200 °C for 4 hours in a current flow of H_2/Ar (1/99).

2 Structural properties

X-ray measurements have been performed at room temperature with a D-max Rigaku system with rotating anode operated at 40 kV and 80 mA and a graphite monochromator was used to select the Cu $K\alpha_{1,2}$ radiation. The X-ray diffraction patterns for all the samples can be indexed in a cubic crystallographic structure and are single phase except for tiny amounts of impurity phases. As an example, we mention that the $x = 0.3$ sample shows a small impurity peak which could correspond to $BaMnO_4$ (positioned at $2\Theta \approx 26°$) and corresponds to less than 2% of the sample scattering. In Figure 1a, we compare the patterns at low angles ($17° \leq 2\Theta \leq 24°$) for $x = 0$, 0.1, 0.2, 0.3. From the positions of the Bragg peaks, we notice that, contrary to the expectation, the lattice parameter is not constant across the series but a slight increase is observed with doping. The lattice parameter at 300 K as a function of La doping, obtained from fits of X-ray diffraction patterns, is shown in Figure 1b. This *unexpected increase* opens up the possibility of an additional contribution to the volume state with doping which arises from changes in the electronic structure. The increase in the electron density at the Fermi level expected with La doping [10,11] could account for the slight increase of the volume in the present series. In fact, a large influence of the electronic state on the volume was evidenced in manganite oxides [12]. This is further discussed in the "discussion" section.

Antisite defects can occur if one Fe atom and one Mo atom exchange their positions, which bring about a decrease in the magnetization [8,13]. If Fe and Mo are randomly distributed on the B site, antisites are 50% and magnetization should be zero. The degree of Fe/Mo ordering can be qualitatively determined in the cubic double perovskite structure by comparing the diffracted intensity ratio $I(111)/I(200)$, as was previously done in a similar way for the tetragonal system Sr_2FeMoO_6 [14]. The (111) reflection is a superstructure peak associated with the Fe/Mo alternative ordering in the double perovskite structure and its intensity decreases with increasing Fe/Mo antisite defects. In our case, however, the intensity of the (200) reflection can vary with doping. By refinement of the whole X-ray diffraction patterns, the amount of antisites has been determined and plotted in the inset of Figure 1b. An increase of antisites with doping is seen beyond the error bars but for the compound with largest doping, $Ba_{1.3}Sr_{0.1}La_{0.6}FeMoO_6$, the antisites are ≈16%. Sánchez et al. studied the influence of antisites in Sr_2FeMoO_6 samples and found that samples with ≈16% of antisites did not show any noticeable increase in T_C [15].

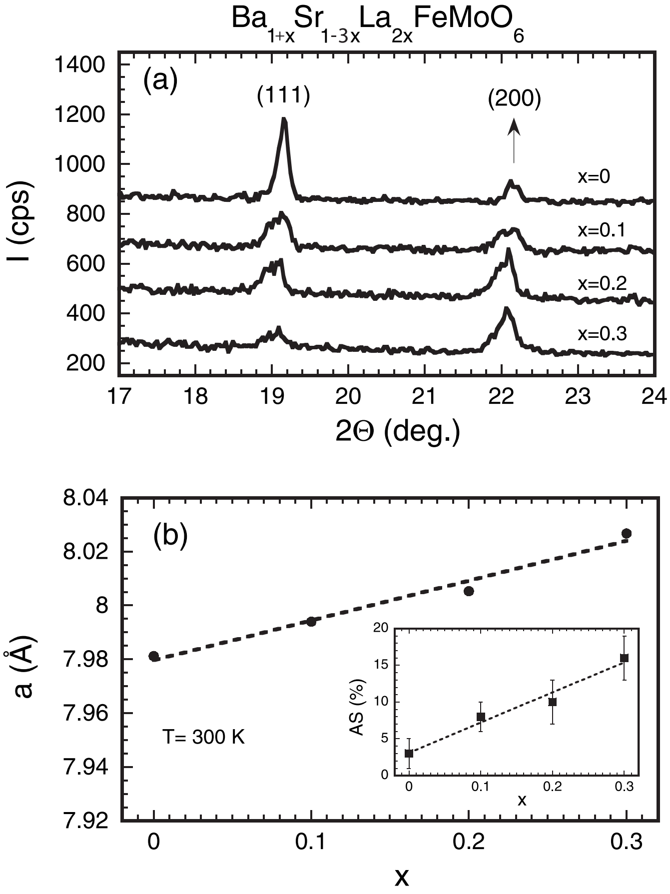

Fig. 1. (a) X-ray diffraction patterns at low angles ($17° \leq 2\Theta \leq 24°$) for all the studied compounds. The intensity of the superstructure peak (111) in the cubic structure, associated with the Fe/Mo ordering, decreases with doping. (b) Lattice parameter as a function of doping at 300 K (obtained from X-ray diffraction refinements). The inset shows the amount of antisites as a function of doping obtained from the same fits.

Neutron diffraction experiments have been carried out on the high-resolution powder diffractometer D2B ($\lambda = 1.6$ Å) and the high-intensity powder diffractometer D1B ($\lambda = 2.52$ Å), both at the ILL, Grenoble (France). Rietveld refinements of the diffraction patterns at 600 K were tried in the $x = 0.1$ sample in order to confirm that we have a good control of the real stoichiometry of the samples. The obtained stoichiometry is [Ba1.11(0.05)Sr0.71(0.05)La0.20(0.05)] [Fe0.9(0.03)Mo0.1 (0.03)] [Mo0.9(0.03)Fe0.1(0.03)] [O5.92(0.05)]. We notice a negligible deviation of the oxygen content (<1.4%) and the presence of 10% of antisites, which is in reasonable agreement with the X-ray diffraction refinements at room temperature.

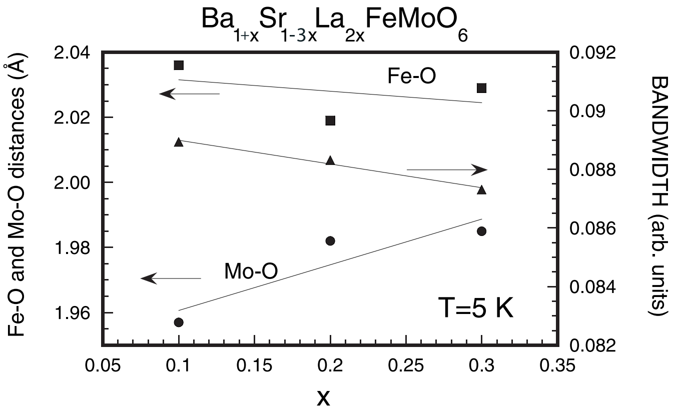

Fig. 2. Fe-O (■) and Mo-O (●) distances at 5 K obtained from neutron diffraction refinements. Taking into account these data, the bandwidth (▲) is tentatively calculated and shown (see text).

We have also performed neutron diffraction experiments on D2B at 5 K in order to get further structural data for the estimate of the change in the bandwidth across the series. All the studied samples (x = 0.1, 0.2, and 0.3) remain cubic at 5 K. In a previous work on AA'FeMoO$_6$ compounds, we estimated the bare electronic bandwidth (W) by using an empirical formula that depends on structural parameters: the Fe/Mo-O distances and the Fe-O-Mo angles [5]. In the present case, with Ba$_{1+x}$Sr$_{1-3x}$La$_{2x}$FeMoO$_6$, W will be given by: $W \propto 1/(\langle d_{\text{Fe/Mo-O}}\rangle)^{3.5}$ because in the cubic structure the Fe-O-Mo angle is 180°. From the refinements at 5 K, we have obtained the Fe-O and Mo-O distances and calculated W (see Fig. 2). We notice that the bare electronic bandwidth slightly decreases across this series. In the previous work on AA'FeMoO$_6$ compounds [5] we found that $T_C \propto W$, which means that from structural effects alone, one would expect a slight decrease in T_C across the Ba$_{1+x}$Sr$_{1-3x}$La$_{2x}$FeMoO$_6$ series. We will see later that the contrary occurs, the large increase in T_C being attributable to the increase in the band filling promoted by La doping.

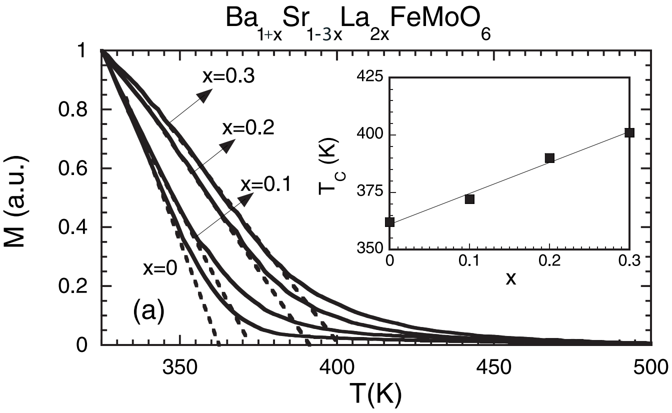

Fig. 3. Magnetization as a function of temperature for all the studied compounds. For a better comparison, the magnetization has been normalised by the value at 325 K. Extrapolation of the curves below T_C (drawn with dashed lines) has been used in order to obtain T_C. The inset shows T_C as a function of doping.

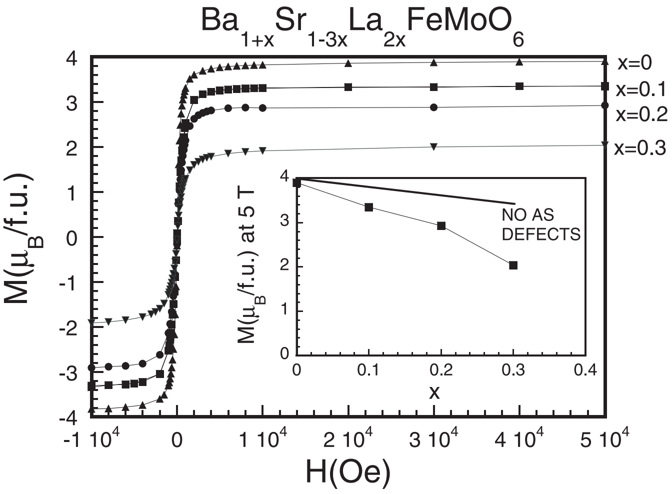

Fig. 4. Magnetization at 5 K for all the studied compounds. The inset compares the magnetization at 5 T and 5 K as a function of doping. Deviations from the straight line (calculated from doping effects alone) are thought to arise from antisite defects.

3 Magnetic behavior

The magnetic behavior has been studied by means of magnetization measurements in a commercial SQUID magnetometer (up to 375 K) and a Faraday balance (up to 500 K). First, we focus on T_C. In Figure 3 the thermal dependence of magnetization for all the compounds (measured with the Faraday balance) is shown. From these measurements, T_C is obtained by linear extrapolation of the magnetization as done in reference [6]. In the inset of Figure 3a we show the doping dependence of T_C. A clear increase in T_C with doping is found: ≈42 K from $x = 0$ to $x = 0.3$, which amounts to about 70 K for an increase from 1 to 2 in the number of electrons per unit formula at the Fermi level. We would like to remark that this increase in T_C cannot be attributed to having strongly Fe/Mo disordered samples. In fact, Sánchez et al. have observed in Sr$_2$FeMoO$_6$ that samples with ~16% of antisites do not show any noticeable increase of T_C [15]. However, they measure larger T_C with samples having 41% of antisites. As a consequence, this source for the observed large increase of T_C can be ruled out in our samples as we are working with samples having antisites equal or less than 16%.

The performed doping and the increasing presence of antisites have a strong impact on the magnetization value as shown in Figure 4. The ferromagnetic interaction in the parent compound BaSrFeMoO$_6$ cubic double perovskite is usually explained as arising from the double-exchange interaction between localized magnetic moments on Fe^{+3} sites ($3d^5$, $S = 5/2$) mediated by itinerant electrons provided by Mo^{+5} ions ($4d^1$, $S = 1/2$). According to band calculations, the $3d$ spin-up subband is full and it is the electron shared in the spin-down subband by Fe and Mo which simultaneously mediates the double-exchange interaction and provides the electrical conduction [1,8]. Within this model, one expects for this compound a saturation magnetization of 4 μ_B/f.u.

In Figure 4 the magnetization curves at 5 K for all the compounds are shown. First, one can notice that for the undoped compound ($x = 0$), the saturation magnetization, 3.9 μ_B/f.u., is slightly below the expected value when no antisite defects are present, 4 μ_B. In fact, only in the $Ba_{1.6}Sr_{0.4}FeMoO_6$ compound this maximum value has been reached [7], the general behavior being that a smaller value is found. As observed in Figure 4, the saturation magnetization strongly decreases with x in $Ba_{1+x}Sr_{1-3x}La_{2x}FeMoO_6$. This decrease is attributed to two different effects. First, due to the presence of La^{+3}, the magnetization will diminish according to the dependence $[5-(1+2x)]$ μ_B, as indicated with a straight line in the inset of Figure 4. The difference between this theoretical value and the real value is attributed to the presence of antisites. As found experimentally in Sr_2FeMoO_6 [14], the presence of antisites reduces the saturation magnetization as $M_S = (4 - 8y)$ μ_B/f.u., where y is the percentage of Fe/Mo antisites (within this model, the absence of Fe/Mo ordering means 50% of antisites and zero magnetization). In the series $Ba_{1+x}Sr_{1-3x}La_{2x}FeMoO_6$, and due to the presence of La, this formula transforms to $M_S = (4-2x-8y)$ μ_B/f.u. If we apply this formula to the experimental results shown in Figure 4, we find that the percentage of antisites is 1.3% for $x = 0$, 5.5% for $x = 0.1$, 8.4% for $x = 0.2$ and 16.9% for $x = 0.3$. This increase in the amount of antisites agrees with the X-ray and neutron diffraction data shown here as well as with NMR results [11]. We remark that a good quantitative agreement is found between the amount of antisites obtained with X-ray diffraction and that one deduced from the magnetization measurements assuming a simple model.

Finally, from the magnetization curves we can extract information on the coercive and saturation fields, which are important in the magnetoresistance properties of polycrystalline samples because low saturation fields favor large low-field magnetoresistance [16,17]. In $Ba_{1+x}Sr_{1-3x}La_{2x}FeMoO_6$ we find as a function of doping no substantial change of the coercive field, which is below 20 Oe in all cases. If we define the saturation field as the field for having 90% of the magnetization measured at 5 T, the saturation field is about 1.5 kOe for $x = 0$, 1.9 kOe for $x = 0.1$, 2.1 kOe for $x = 0.2$, and 5.4 kOe for $x = 0.3$. We can consider that these materials are rather soft in sharp contrast with other magnetic double perovskites like Re-based ones [2,18].

4 Magnetotransport properties

Single-crystals of double perovskites show metallic resistivity with absolute value in the range of $\sim 10^{-4}$ Ω cm [19]. As a consequence, the intrinsic "bulk" behavior is metallic. However, polycrystals of these materials can show semiconducting or metallic behavior depending on the synthesis procedure and the absolute values of resistivity can range from those of single crystals to several orders of magnitude higher [20]. The extrinsic contribution is usually named intergrain resistance. In Figure 5a the thermal dependence of d.c. resistivity for $x = 0.1$, 0.2, and 0.3 is shown. In all cases, the resistivity is found to be in the range of $\sim 10^{-2}$ Ω cm and varies little with temperature. This means a substantial contribution of intergrain resistance and intergrain magnetoresistance effects can be anticipated. As the absolute value of resistivity changes little from $x = 0.1$ to $x = 0.3$, as a function of doping we do not expect any substantial change of microstructural parameters influencing the magnetotransport properties like the grain size, grain connectivity, etc.

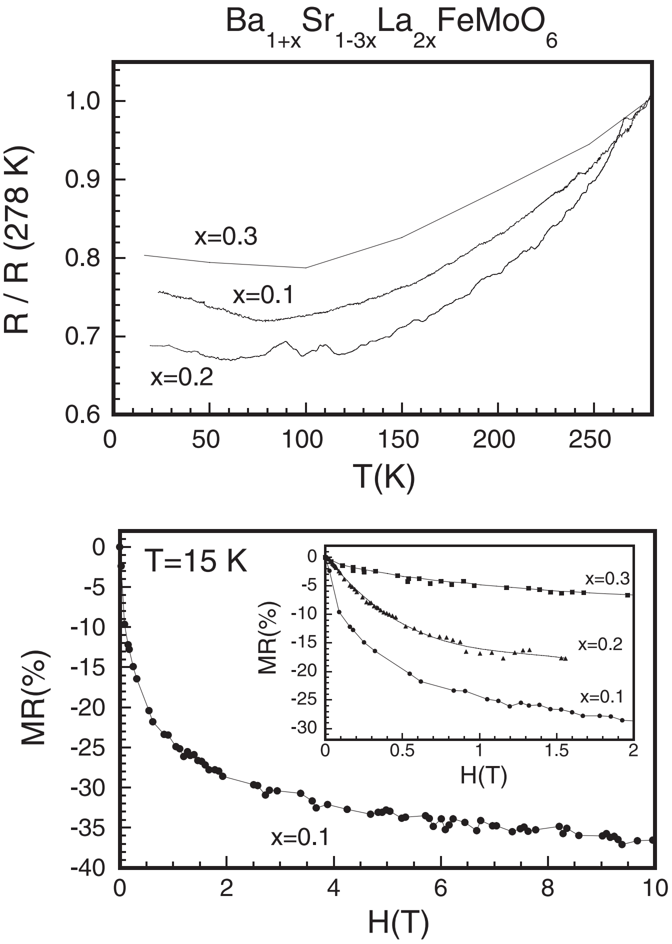

Fig. 5. (a) Thermal dependence of the normalized resistance for $x = 0.1$, 0.2 and 0.3. The absolute value of resistivity is $\sim 10^{-2}$ Ω cm in all cases. (b) Magnetoresistance at 15 K, defined as $MR(\%) = 100^{*}[R(H) - R(0)]/R(0)$, for $x = 0.1$, 0.2 and 0.3.

One of the most remarkable properties of polycrystalline double perovskites was the discovery of a large magnetoresistance [1] which is usually explained by the "intergrain magnetotunnelling" effect [21]. This mechanism is based on the fact that the grain boundary resistance can be modulated by an applied magnetic field if the conduction between grains proceeds via spin-dependent tunneling, which leads in some cases to a large magnetoresistance. This occurs because at zero field the magnetization of neighboring grains is misaligned, which is a higher resistance state than having parallel magnetization between grains above the saturation field. A high spin polarization at the Fermi level is required to obtain large magnetoresistive effects as is the case of double perovskites like Sr_2FeMoO_6 [1]. Experimentally, together with the magnetoresistive effect ocurring below the saturation field (low-field magnetoresistance) there exists a high-field magnetoresistive effect which is thought to arise from the non-saturated magnetic state of the surface of the grains [22].

In Figure 5b the magnetoresistance at low temperature is shown for $x = 0.1$, 0.2, and 0.3. A large magnetoresistance is observed in all cases but the magnitude decreases with doping. As normally found in systems showing intergrain magnetoresistance, these compounds show a rapid decrease of resistance at low fields and a slower decrease at higher fields. The magnetoresistance is not saturated at the maximum measured field of 10 T. Both, the low-field and the high-field magnetoresistance, decrease with doping. One first reason to justify the decrease of magnetoresistance with doping is the increase in the saturation field (shown in the previous section), which makes more difficult to align the magnetization of the grains with the field. A second reason is the increase of antisites with doping. In fact, García-Hernández et al. have found that the low-field magnetoresistance diminishes as the amount of antisites increases [23]. We think that antisites act as magnetic impurities and, as a consequence, are strong magnetic scattering centers that produce spin memory loss. Taking into account that in double-exchange systems the spin diffusion length is small and the fact that a high spin polarization at the grain surface is a prerequisite for observing intergrain magnetoresistance, it is plausible that antisites decrease the degree of spin polarization of the conduction electrons reaching the surface grain.

5 Discussion and conclusions

The aim of the present study was to clarify the role of the electronic bandfilling alone in the Curie temperature of Fe/Mo-based double perovskites. Previous studies suffered from additional effects like changes in the crystallographic structure, the bare electronic bandwidth, substantial increase of antisites, etc. [6,7]. By synthesis of the series $Ba_{1+x}Sr_{1-3x}La_{2x}FeMoO_6$, the designed combination of cations has allowed the minimization of structural changes and an effective increase of the number of electrons in the conduction band.

We have found that the crystallographic structure remains cubic as checked with X-ray and neutron diffraction, even at 5 K. The lattice parameter increases slightly with doping, which seems to correlate with changes in the electronic structure induced by La doping. As La^{3+} substitute Sr^{2+}, the extra electrons going into the conduction band will modify the density of states at the Fermi level [10,11]. These electrons can modify the bonding lengths through screening of the ionic potentials that determine the interatomic distances. A clear example of the influence of the electronic state on the volume state occurs in manganite perovskites [12]. In those compounds the localized or itinerant character of the Mn outermost electrons brings about different volume states and strong anomalies in the volume thermal expansion.

From neutron diffraction refinements, we have obtained relevant structural parameters that have allowed us to calculate the change in the bare electronic bandwidth with Ba/La doping. We have found that with doping the bandwidth diminishes and, as a consequence, cannot be responsible for the found increase in T_C [5]. Another possible source of T_C enhancement can be a substantial increase in the number of antisites, which is not the case in the studied series. We have found that the maximum number of antisites is $\sim$16% for $x = 0.3$ and, according to the experimental studies of Sánchez et al. [15], this value is not able to produce the large increase in T_C observed in our case.

Once these extrinsic effects discarded, the plausible scenario is that the increase of the number of conduction electrons promoted by La doping enhances the double-exchange magnetic interaction. In this mechanism, the conduction electrons align antiparallel to the localized Fe magnetic moments ($S = 5/2$) and transmit the information about this magnetic state to the neighbouring Fe ions. It seems that the double-exchange mechanism strengths up to the studied doping level (1.6 conduction electrons per unit formula), which should be considered in theoretical models of these systems. Magnetization and magnetotransport properties have been explained taking into account the increase of the spin-down subband electrons at the Fermi level and the moderate rise in antisites as a function of doping.

An open question is why the performed Ba/La doping on Sr leads to an increase of the amount of antisites. One possible explanation can be based on the fact that the La doping mainly rises the density of states of Mo as shown by NMR [11] and photoemission experiments [10]. This would increase the volume of the MoO_6 octahedra and, consequently, the size of FeO_6 and MoO_6 octahedra approached, as experimentally shown in Figure 2. Not too dissimilar sizes of FeO_6 and MoO_6 octahedra paves the way for the creation of Fe/Mo antisites.

In conclusion, these results clarify the role played by the electronic bandfilling alone in the increase of T_C in Fe/Mo-based double perovskites and are a stringent test for theoretical model describing these compounds.

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