

NMR and X-MCD study of $\text{Sr}_{1-3x}\text{Ba}_{1+x}\text{La}_{2x}\text{FeMoO}_6$

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Abstract

A study of La influence on molybdenum and iron magnetic states in the $\text{Sr}_{1-3x}\text{Ba}_{1+x}\text{La}_{2x}\text{FeMoO}_6$ series ($x = 0, 0.1, 0.2, 0.3$) is reported. The main line and a low frequency satellite of the Mo NMR spectra are attributed to ideal and defect sites. The structure of the main line with increasing La content indicates a local effect of electron doping on Mo sites. Fe:K edge X-ray magnetic circular dichroism spectra show an increased polarisation of the Fe 4p states with La doping. The Fe:K absorption edges show an unchanged Fe ionic state but an increased localisation of the Fe electronic states.

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The family of perovskite compounds has recently been a subject of intensive study owing to their extraordinary structural, magnetic and electronic properties. The Fe–Mo double perovskites are known as half-metallic ferromagnets (ferrimagnets) with a relatively high transition temperature ($T_C > 400$ K) and a significant low field magnetoresistance at room temperature [1]. Neutron diffraction and nuclear magnetic resonance (NMR) measurements have proven the existence of a magnetic moment at the Mo site [2,3]. La substitution was found to increase the Curie temperature and also the number of defects [4].

In order to study the La influence on the Mo and Fe electronic and magnetic state an NMR, X-ray absorption and X-ray magnetic circular dichroism (X-MCD) study of the $\text{Sr}_{1-3x}\text{Ba}_{1+x}\text{La}_{2x}\text{FeMoO}_6$ ($x = 0, 0.1, 0.2$

and 0.3) series has been carried out. The change of Sr/Ba ratio with x was chosen in order to keep constant bandwidth that depends on the Fe–O–Mo angle and the Fe/Mo–O distances. Powder samples were prepared by a solid-state reaction. X-ray diffraction showed them to be single phase of double perovskite structure with less than 2% of spurious phases. Magnetization measurements carried out at 5 and 77 K show a decrease of the saturation moment with La doping from 3.36 ($x = 0.1$) to 2.04 μ_B /f.u. ($x = 0.3$) at 5 K and from 3.23 ($x = 0$) to 1.64 μ_B /f.u. ($x = 0.3$) at 77 K.

The Mo NMR spin echo measurements have been carried out at 4.2 K with no applied field with a frequency swept spectrometer [5]. The spectra, Fig. 1, show a main line and a low frequency satellite which are attributed to the ideal and defect (antisite neighbours and antiphase boundaries) sites, respectively. Both lines consist of ^{95}Mo and ^{97}Mo resonances which are unresolved due to their very close gyromagnetic ratios. With La doping both lines broaden, shift to higher frequencies and a structure appears, which is attributed to La influence through local electron doping. The

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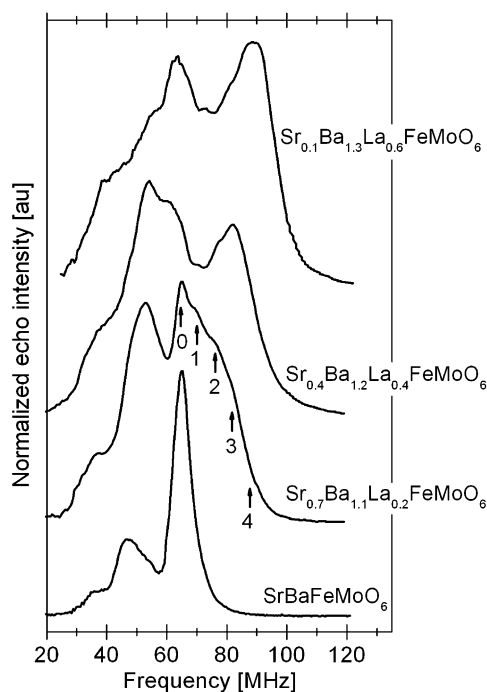


Fig. 1. The Mo NMR spin echo spectra at 4.2 K. Satellites corresponding to 0,1,2,... La neighbours to Mo atoms are marked.

overall shift corresponds to an increase of the Mo moment and the related 4d electron density at the Mo sites. The satellite structure corresponds to Mo ions surrounded by different amounts of La next neighbours and indicates a localised character of electron doping. The hyperfine field at the ideal Mo sites increases from 21.8 T for $x = 0$ to 31.4 T for $x = 0.3$.

From the values of the hyperfine field the corresponding Mo magnetic moments can be determined in a way similar to that in Ref. [3] as $0.55 \mu_B$ for $x = 0$ and $0.79 \mu_B$ for $x = 0.3$. The relative increase of the intensity of the low frequency satellite corresponds to an increase of the number of antisite defects and is consistent with the decreasing saturation magnetisation, as the moments of antisite Fe atoms of $5 \mu_B$ couple antiparallel to the Fe neighbouring moments [6].

X-ray absorption and X-MCD spectra at the Fe:K edge have been measured for $x = 0, 0.2$ and 0.3 (Fig. 2). The position of the absorption edge corresponds to the Fe valence significantly departed from that of $3+$ in Fe_2O_3 toward lower energies. This does not change with La doping, which means an unchanged ionisation state and proves intermediate valence states of Fe and, consequently, Mo. This constitutes an additional confirmation of the DE-like model of electronic and magnetic properties of the compounds [1]. A more

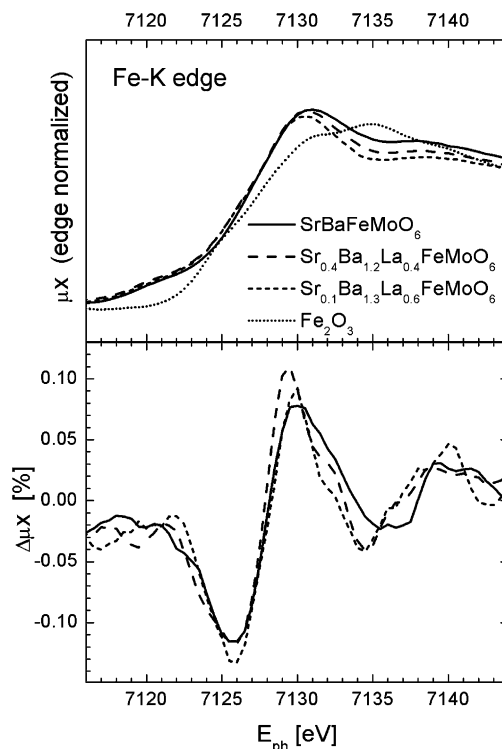


Fig. 2. The X-ray absorption (upper window) and X-MCD (lower window) spectra at the Fe:K edge for $x = 0.0, 0.2$ and 0.3 .

pronounced white line observed for compounds with large La content indicates an increased degree of localisation of Fe electronic states.

The Fe K edge X-MCD spectra, which correspond to the transition of 1s electrons to empty 4p states, show a derivative-like shape of the signal. An increase of the signal with La doping is observed which indicates an increased splitting of the Fe 4p states due to the exchange interaction of 3d electrons.

In conclusion, NMR, X-ray absorption and X-MCD provide the following information on the influence of La doping on the Mo and Fe electronic and magnetic states:

- an extra electron density is introduced locally and is transferred mainly to the adjacent molybdenum sites, leading to an increase of the Mo magnetic moment and
- the iron ionisation state is unchanged but the localisation of the electronic states increases and so does the splitting of the 4p states due to the exchange interaction with 3d electrons.

The increase of localisation may be related to the decrease of bandwidth due to the increasing population of defect sites or due to Coulomb repulsion produced by

the increasing number of electrons in the conduction band.

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