Sr_2FeMoO_6 Double Perovskites and the Effects of Electronic Doping by La Substitution

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We have prepared $Sr_{2-x}La_xFeMoO_6$ samples with various amount of Lanthanum from x = 0 to 0.5. Magnetic and transport measurements show that the magneto-resistance, degree of electronic spin polarization and the saturation magnetization are correlated with the amount of anti-site disorder rather than the changing carrier concentration.

1. Introduction

There has been recent interest in the half-metallic double perovskites of the type $A_2BB'O_6$ due to their large magneto-resistance and high Curie temperatures [1]. These properties indicate that this compound has potential magneto-electronic applications [2]. Band structure calculations predict 100 % spin polarization at the Fermi level with an admixture of $Mo(t_{2g})$ and $Fe(t_{2g})$ orbitals containing down-spin itinerant electrons while the up-spin Fe^{3+} $3d^5$ electrons are localized within $Fe(t_{2g})$ and (e_g) orbitals [1]. Several mechanisms have been proposed to explain the half-metallicity and high Curie temperature but there are some experimental results that question the existing models [3].

2. Experimental details

Double perovskite polycrystalline samples were prepared by a solid-state reaction method from stoichiometric mixes of $Sr(NO_3)_2$, Fe_2O_3, MoO_3 and $La(NO_3)_2 \cdot 6H_2O$. The pellets were placed in air at 1200 ^{o}C and then sintered at 1100 ^{o}C in an atmosphere of 5% H_2 – 95% N_2 [4]. X-ray diffraction (XRD) measurements showed that all samples were single phase to within the limit of detectibility. Magnetization measurements were conducted up to 6 T and 700 K using a Superconducting QUantum Interference Devices (SQUID) magnetometer. The magneto-resistance (MR) was measured using the four terminal method in a magnetic field up to 0.8 T. Zero-field nuclear magnetic resonance (ZFNMR) measurements were made a TecMag spectrometer and a Janis continuous flow cryostat. The spectra were obtained at discrete frequency steps using a Hahn echo sequence, $\tau_{\pi/2}\text{-}\tau\text{-}\tau_{\pi}\text{-}\tau$ where the pulses $\tau_{\pi/2}$ and τ_{π} were 1 μs and 2 μs respectively and τ (20 μs) was the time between the pulses.

3. Results

There is an increase in the amount of anti-site disorder (ASD) with increasing La concentration as estimated from the relative intensities of the (111) superstructure and the (220) XRD peaks [4]. The ASD provides information about the Fe and Mo ordering from perfect ordering (0%) to complete disorder (50%). Fig. 1(a) shows the magnetization at 6 T from 10 to 300 K. We have fitted the low temperature magnetization data to $M(T) = M_0(1 - a_0 T^n)$ and found $n = 1.5$ for all the La-concentrations. This value is expected in the 3D Heisenberg model. In addition, we observed a small variation in a_0. The inset of

Fig.1(a) clearly shows that the saturation magnetization is directly correlated with the amount of ASD, which has also been observed by other groups in pure compound [5,6].
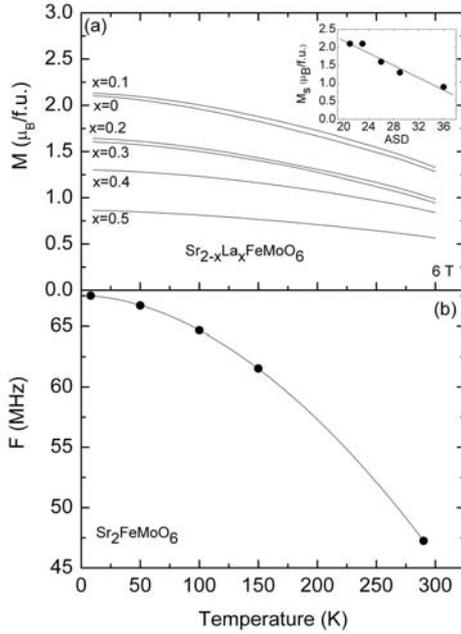

Fig. 1. (a) Temperature dependence of the magnetization in units of Bohr magnetons, μ_B, per formula unit (f.u.) at 6 T. Inset: saturation magnetization at 10 K versus ASD for the $Sr_{2-x}La_xFeMoO_6$ samples. (b) The ZFNMR peak frequency against temperature for the pure sample.

The ZFNMR spectra in the pure compound are similar to those in a previous report and the spectra are believed to be dominated by hyperfine coupling from a static moment on the Mo site to the Mo nucleus [7]. The resultant ZFNMR peak frequency is plotted in Fig. 1b and fitted to $F = F_0 (1 - b_0 T^n)$. We find that $n = 1.84$, which is significantly different from the $n = 1.5$ observed in the magnetization data.
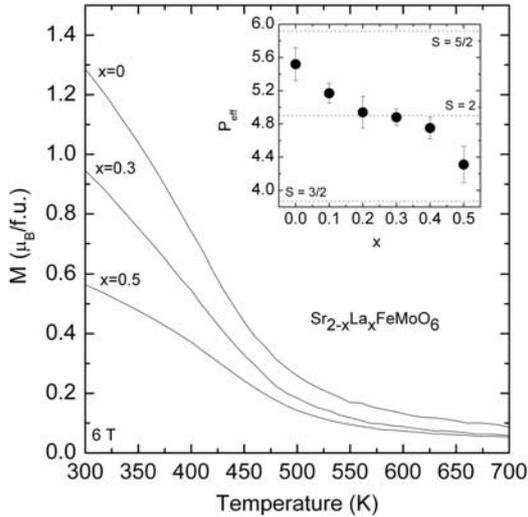

Fig. 2. Magnetization against temperature at 6 T Inset: effective moment versus La concentration. Dotted lines are the theoretical values for S = 5/2 (Fe^{3+}), S = 2 ($Fe^{2+/4+}$), and S = 3/2 for comparison purpose.

Fig. 2 shows the high temperature magnetization data. As can be seen from the inset, the effective moment, P_{eff}, measured in the Curie-Weiss region drops systematically with increasing La-doping from 5.52 to 4.31. By comparing the theoretical and experimental data, it is evident that the change in P_{eff} cannot originate from only the Fe valence.

The magneto-resistance can be written as $MR = -\Delta\rho / \rho = (\rho(0) - \rho(H)) / \rho(0)$ where $\rho(0)$ is the resistivity measured without any magnetic field and $\rho(H)$ is the resistivity under

an applied magnetic field. As can be seen from Fig. 3, there is a systematic drop in the MR with increasing electronic doping by La. The MR can be modelled by a spin dependent tunnelling across an intergranular insulating region term, $-\gamma^2 m(H)^2$, and an intragranular term αH, where γ is the degree of spin polarization, $m(H)$ is the magnetization divided by the saturation magnetization and α is field-independent [8,9]. We found that γ determined by fitting the MR to this model correlates well with the amount of ASD (Fig. 3 inset). Low values of γ at room temperature are also observed in the pure compound by other researchers and it has been attributed to a disordered region near the grain boundary that decreases γ below that expected from the bulk intragranular region [9].
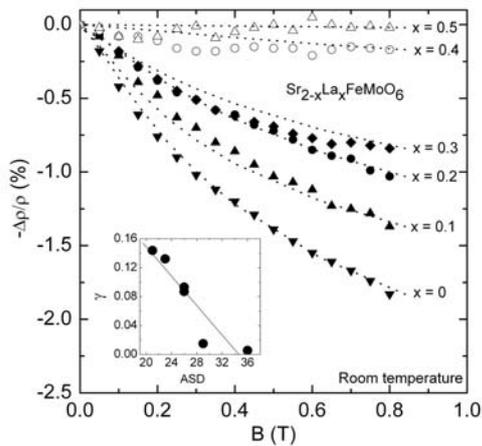

Fig. 3. Magneto-resistance versus applied magnetic field at room temperature. The dotted curves are fits to the spin dependent tunnelling model [9]. Inset: Spin polarization versus ASD.

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