Magnetization and specific heat of La doped Sr_2FeMoO_6

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Abstract

We present high-temperature magnetization and low-temperature specific heat measurements performed on the electron doped double perovskite $Sr_{1.7}La_{0.3}FeMoO_6$. We have obtained the electronic contribution to C_p, $\gamma = 11.5(5)$ mJ/mol K^2. The electronic susceptibility, derived from the magnetic measurements in the paramagnetic regime ($T > T_c = 390$ K), was $\chi_e^0 = (4.9 \pm 1.5) \times 10^{-4}$ emu/mol. Antiferromagnetic coupling between localized and itinerant moments was inferred from the data, with a coupling constant $\lambda = -(475 \pm 50)$ mol/emu, that results in a ferromagnetic-like Curie–Weiss susceptibility with $\Theta = 390(5)$ K. These results are compared with those obtained for the undoped material.
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The double perovskite Sr_2FeMoO_6 is a conducting ferromagnet below $T_c = 400$ K, that is magnetoresistant at room temperature. In a previous work [1], a magnetic study in the paramagnetic (PM) phase of the compound was reported. In that paper, the PM susceptibility was well described in terms of two interacting magnetic sublattices: the localized Fe^{3+} (3d^5) cores and the delocalized electrons. A strong antiferromagnetic (AFM) coupling between the two systems results in a reduction of the effective moment, μ_{eff}, of the Fe^{3+}. We note that, at variance with classical ferrimagnets, a Curie–Weiss (CW) T dependence is observed [1] with a ferromagnetic-like CW temperature, Θ. A bare susceptibility independent of T, $\chi_e^0 = 3.7 \times 10^{-4}$ emu/mol for the itinerant electrons was derived from the experimental data.

Doping of this double perovskites by substitution of Sr^{2+} for La^{3+} has been observed [2] to raise the Curie temperature, what is relevant for potential technological applications. In this paper, we present a study on the high-temperature magnetic properties and low-tempera-

ture specific heat measurements for samples of La doped Sr_2FeMoO_6, in the low doping regime ($\leqslant 30\%$).

Samples of Sr_2FeMoO_6 and $Sr_{1.7}La_{0.3}FeMoO_6$ were prepared from pure oxides following the solid-state reaction method. The samples were calcinated at 950°C in air during 24 h followed by a reduction at 900°C in a 10% H_2–Ar mixture for 1 h. This procedure was repeated several times. The final heat treatment was performed under ultra-high vacuum (10^{-6} Torr) at 1200°C during 12 h. Powder XRD patterns indicated the presence of single-phase materials with the tetragonal I4/mmm symmetry for both samples. The lattice parameters were $a = 5.579(3)$ Å and $c = 7.904(3)$ Å for Sr_2FeMoO_6, while those of $Sr_{1.7}La_{0.3}FeMoO_6$ were $a = 5.585(3)$ Å and $c = 7.788(3)$ Å.

The magnetization, $M(T)$, was measured with a Faraday-balance magnetometer between 250 and 1200 K. Specific heat C_p measurements were made in the 0.45–3 K range by a pulsed method in a semiadiabatic calorimeter equipped with a He^3 cryostat.

For $Sr_{1.7}La_{0.3}FeMoO_6$, we have measured $M(T)$ vs. H, in 20 K steps for $H \leqslant 12.5$ kG, in air with $p < 1$ Torr. In order to control the reversibility we repeated the measurements at 473 K after each temperature step. We found irreversible changes for $T > 700$ K, as in the

undoped sample [1]. Thus, we considered only data for $T < 700$ K. For the highest fields, we observed a linear dependence of the type: $M(T) = M_0(T) + \chi(T)H$. Around 400 K, $M_0(T)$ presents a rapid increase with decreasing T, signalling the FM transition at $T_c = 390$ K (see Fig. 1). Above T_c a small and weakly T dependent M_0 ($\approx 0.15 \mu_B$/f.u.) remains up to $T \approx 700$ K. This small contribution is compatible with the presence of tiny amounts of metallic Fe impurities [1] possibly appearing because of the severe reducing conditions required for the sample preparation. Below ≈ 375 K, different behaviors are observed according to heating and cooling conditions.

In the inset, we show $\chi^{-1}(T)$ vs. T. We observe a CW behavior with $C = 2.75(20)$ emu-K/mole and $\Theta = 390(5)$ K. We describe the system in terms of coupled localized and intinerant electrons using the Vonsovsky–Zener model [1]. In this case, the total $\chi(T)$ is CW like with $C = C_{Fe}(1 + \lambda \chi_e^0)^2$ and $\Theta = C_{Fe}\lambda^2\chi_e^0$. We obtain for the bare susceptibility of the mobile electrons $\chi_e^0 = (4.9 \pm 1.5)10^{-4}$ emu/mol. A coupling coefficient, $\lambda = -(475 \pm 50)$ mol/emu, indicates a strong AFM interaction between the itinerant and the localized moments. Comparison with the undoped material [1] indicates only a small increase in χ_e^0.

The specific heat is shown in Fig. 2 for Sr_2FeMoO_6 and $Sr_{1.7}La_{0.3}FeMoO_6$ for $T < 3$ K. We observe that C_p/T is slightly smaller for the doped sample in this temperature region, but converge to approximately the same value for $T \to 0$, $\gamma = 11.5(5)$ mJ/mol K^2, associated with the electronic contribution. This result is in agreement with previous reports [3] in spite of the differences in the sample preparation methods. A fit of the experimental data to $C_p(T) = \gamma T + \beta T^3$ gives, for the lattice contribution: $\beta = 1.3(1)$ mJ/mol K^4 for $Sr_{1.7}La_{0.3}FeMoO_6$ and $\beta = 1.7(1)$ mJ/mol K^4 for Sr_2Fe-MoO_6. The corresponding Debye temperatures are $\Theta_D = 250$ K and 230 K, respectively, if we consider 10 atoms per formula unit.

Fig. 2. $C_p(T)/T$ vs. T^2 for Sr_2FeMoO_6 and $Sr_{1.7}La_{0.3}FeMoO_6$.

Two parameters derived from our data, γ and χ_e^0, are expected to be proportional to the density of states in the Fermi level, $N(E_F)$. We derived $N(E_F) = 5$ states/eV-f.u. from the measured γ. The experimental ratio $\gamma/\chi_e^0 = 2.4 \times 10^4$ mJ/emu K^2 may be compared to the theoretical value, $\gamma/\chi_e^0 = (\pi k_B/\mu_B)^2/3 = 7.3 \times 10^4$ mJ/ emu K^2. This comparison indicates a Stoner enhancement parameter, for χ_e^0, of about 3, similar to the values observed in other oxides. This is a nice agreement, since it supports our model for the high-temperature itinerant susceptibility, derived in a rather indirect way. The similarity between the γ values for doped and undoped materials may indicate that, in spite of the electron doping, $N(E_F)$ remains almost unchanged, at least for concentrations where the I4/mmm tetragonal structure is preserved. Note that, for La concentration above $x = 0.4$, the crystalline structure changes from tetragonal to monoclinic or orthorhombic [2]. It is in this range of x where the largest shifts of T_c were observed. Thus, it will be interesting to extend the present study to materials with higher levels of doping.
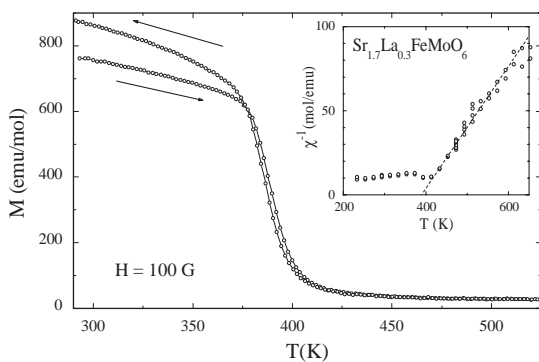
Fig. 1. $M(T)$ vs. T, as measured for $H = 100$ G. Inset: $\chi^{-1}(T)$ vs. T, derived from the linear $M(H)$ dependence for $H > 8$ kG.
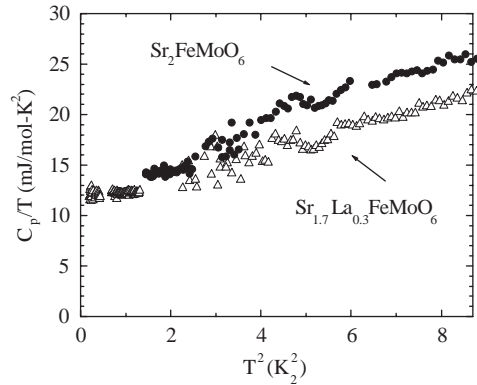
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