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Ferromagnetic coupling strength and electron-doping effects in double perovskites

J. Fontcuberta[a,*], D. Rubi[a], C. Frontera[a], J.L. García-Muñoz[a], M. Wojcik[b], E. Jedryka[b], S. Nadolski[b], M. Izquierdo[c], J. Avila[c], M.C. Asensio[c]

[a]*Instiut de Ciència de Materials de Barcelona, CSIC, Universitat Autonoma de Barcelona, Campus Univ. Autonoma de Barcelona, Belaterra 08193, Catalunya, Spain*

[b]*Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02 668 Warszawa, Poland*

[c]*LURE, Centre Universitaire Paris Sud, Bât 209D, 91405 Orsay, France & Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco 28049 Madrid, Spain*

Abstract

We review experiments and results on ferromagnetic and metallic A_2FeMoO_6 double perovskites that made it possible to obtain a detailed understanding of the nature of the ferromagnetic coupling and paved the way for further enhancement of the Curie temperature. We show that appropriate chemical substitutions, combined with detailed structural, magnetotransport and spectroscopic data allow us to map quite a complete picture of the properties of these oxides.

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1. Introduction

Ferromagnetic coupling in half-metallic $L_{1-x}A_xMnO_3$ manganites is commonly described by the so-called "double exchange model". Within this scenario, the electronic configuration of Mn ions rapidly fluctuates between Mn^{3+} and Mn^{4+} states and the Curie temperature ($T_C \leqslant 360\,K$) is determined by the hole concentration in the conduction band and its bandwidth (W). Double perovskites (DP), such as A_2FeMoO_6 ($A = Sr$, Ca, Ba), are also half-metallic ferromagnets that are receiving much attention [1] due to the fact that their Curie temperature is even higher than that of manganites making them more promising materials for applications. $A_2MM'O_6$ double perovskites are built up by alternate $M'O_6$ and MO_6 octahedral units bonded by oxygen bridges, where A is an alkaline earth or rare-earth ion and M, M′ are 3d and 4d/5d transition metals. In short, the electronic configuration of Sr_2FeMoO_6 (SFMO) can be described by Fe($3d^{6-\delta}$):Mo($4d^{\delta}$) ($\delta \approx 0.3$ [2,3]). The electrons in Fe-3d fully-filled (t_{2g}^3 and e_g^2) spin-up bands can be viewed as localized whereas the Fe 3d partially empty ($t_{2g}^{1-\delta}$) spin-down states are strongly hybridized with O-2p orbitals and partially empty Mo-$4d^{\delta}$ (spin-down) states. Consequently, these transition-metal oxides are characterized by bands associated to one spin polarization (in this case, Fe-3d "spin-up") entirely filled, which are

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*Corresponding author. Tel.: +34 93 580 18 53; fax: +34 93 580 57 29.
E-mail address: fontcuberta@icmab.es (J. Fontcuberta).

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separated from unoccupied bands of the same symmetry by a bandgap located at the Fermi level. The other spin channel involving Fe-3d and Mo-4d "spin-down" electrons has a metallic character. Magnetic measurements are consistent with ferromagnetic ordering of Fe($3d^{6-\delta}$) moments which shall be antiferromagnetically coupled to any moment on Mo($4d^{\delta}$) sites.

However, understanding the physical mechanism responsible for the ferromagnetic ordering remains challenging [4]. Difficulties arise mainly due to the fact that in this structure the 4d(Mo) ions are essentially non-magnetic and thus the separation between the magnetic ions (3d(Fe)) is substantial (~8 Å). In spite of this, the Curie temperature is very high (up to ~500 K), exceeding that of the celebrated manganites. This observation suggests that the Double Exchange model used to describe the ferromagnetism in manganites may not be valid in the case of $A_2MM'O_6$ double perovskites.

It has been recently shown [5] that the magnetic properties of Sr_2FeMoO_6 in the paramagnetic regime cannot be understood by considering only the contribution of localized moments: the effective paramagnetic moment is found to be smaller than expected for any of electronic configurations: Fe($3d^6$)–Mo($4d^0$) or Fe($3d^5$)–Mo($4d^1$). Magnetization data have been modeled [6] by assuming that there is an exchange-induced spin polarization of the conduction band being antiferromagnetically coupled to the localized moments by Hund coupling. Even more, the strength of the ferromagnetic coupling has been predicted to be proportional to the density of states at the Fermi level ($D(E_F)$) and thus T_C can be increased by electron doping [6]. Subsequent experiments [7–10] have confirmed this prediction. Moreover, it has been experimentally shown that the rise of T_C is accompanied by an enhancement of the density of states at the Fermi level (mainly its projection onto Mo-based states) [11]. In agreement with this finding, recent ^{95,97}Mo nuclear magnetic resonance (NMR) experiments on electron-doped $Sr_{2-x}La_xFeMoO_6$ have shown that there is a clear correlation between the Curie temperature and the magnetic moment of Mo ions [12].

However, these experimental findings sharply contrast with certain recent theoretical predictions, anticipating a reduction rather than an enhancement of the Curie temperature upon electron doping of these oxides [13,14]. This illustrates the limitations of our understanding of the physics behind these materials. A possible reason for this dramatic discrepancy is that the theory has been developed assuming electronic rigid-band models and neglecting the fine structure aspects. The different cationic sizes of the substituting ions certainly modify the structure and thus the comparison with models may not be appropriate.

To overcome this difficulty, heterovalent atomic substitution experiments in the DP structure but restricted to species having the same ionic size are required. To this extend, the $Ca_{2-x}Nd_xFeMoO_6$ series appears to be optimal as the size of Nd^{3+} (1.11 Å) and Ca^{2+} (1.12 Å) are virtually identical and thus steric effects shall be minimized.

In this article we shall review key experiments used to build the picture which we have described and report detailed new data on electron doping in the $Ca_{2-x}Nd_x$-$FeMoO_6$. We will conclude by demonstrating that pure electron filling largely dominates the observed rising of the Curie temperature and thus the strength of the ferromagnetic coupling.

2. Experimental

Ceramic samples of $Nd_xCa_{2-x}FeMoO_6$, with $x = 0$, 0.2, 0.4, 0.6 and 0.8, were synthesized by standard solid-state reaction as described elsewhere [10]. The structural characterization was done by means of X-ray powder diffraction (XRPD, Cu $K_{\alpha 1,\alpha 2}$ radiation). Neutron powder diffraction (NPD) studies were performed at the Institute Laue-Langevin (ILL, Grenoble) at the D1B ($\lambda = 2.52$ Å) diffractometer from room temperature (RT) to well above T_C. Rietveld refinements of XRPD data were done using FullProf software, to determine the concentration of antisites (misplaced Fe(Mo) ions at Mo(Fe) sites). XRPD and NPD data collected at RT have been jointly refined in order to determine the changes of the structural parameters upon doping. Magnetic characterization was performed by using a Quantum-Design SQUID magnetometer (2–300 K, up to 5.5 T). Magnetic measurements above room temperature were made by using a vibrating sample magnetometer (VSM). The magnetotransport properties have been measured in a PPMS system from Quantum Design. Microscopic characterization of charge and spin distribution around Mo has been carried out using NMR technique. ^{95,97}Mo NMR experiments have been performed at 4.2 K in zero external magnetic field using a coherent, phase sensitive spin echo spectrometer. The NMR spectra have been recorded every 1 MHz in the frequency range 20–140 MHz and corrected for the intrinsic enhancement factor which was experimentally determined at each frequency point from the RF power dependence of spin echo signal intensity. Photoemission experiments [11] have been performed, at room temperature, at the SU8 beamline at LURE using synchrotron radiation light.

3. Results and discussion

We first show in Fig. 1 the temperature dependence of the paramagnetic magnetic susceptibility (χ) of the