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Author(s):   Lindén, J. & Yamamoto, T. & Karppinen, Maarit & Yamauchi, H. & Pietari, T.

Title: Evidence for valence fluctuation of Fe in Sr[sub 2]FeMoO[sub 6-w] double perovskite

Year: 2000

Version: Final published version

Please cite the original version:

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J. Lindén, T. Yamamoto, M. Karppinen, H. Yamauchi, and T. Pietari

Evidence for valence fluctuation of Fe in Sr$_2$FeMoO$_{6-w}$ double perovskite

J. Lindén,[a] T. Yamamoto, M. Karppinen,[b] and H. Yamauchi[c]
Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

T. Pietari
Department of Technical Physics, Helsinki University of Technology, FIN-02015 Espoo, Finland

In this letter evidence for the formation of a valence-fluctuation state of iron, formally denoted as Fe$^{2.5+}$, is presented. The system under study is the Sr$_2$FeMoO$_{6-w}$ double perovskite, known for exhibiting a very large magnetoresistance. Samples of Sr$_2$FeMoO$_{6-w}$ were synthesized by means of an encapsulation technique utilizing an Fe getter technique and characterized by ^{57}Fe Mössbauer spectroscopy. From 5 K to room temperature the Mössbauer spectrum is dominated by a component with hyperfine parameter values between those expected for high-spin Fe^{3+} and high-spin Fe^{2+}. © *2000 American Institute of Physics.* [S0003-6951(00)00520-9]

Recently, spin-polarized giant tunneling magnetoresistance was confirmed at room temperature in powder samples of the Sr$_2$FeMoO$_{6-w}$ double-perovskite system.[1] The origin of the magnetoresistance (MR) effect is claimed to be in the half-metallic nature of Sr$_2$FeMoO$_{6-w}$. By applying a magnetic field to a specimen, the scattering of spin-polarized charge carriers at magnetic domain walls is strongly suppressed.[1] The absence of strong MR effects in single crystals of Sr$_2$FeMoO$_{6-w}$ supports this notion.[2] This and similar perovskite systems were characterized already more than 30 years ago.[3–5] The recent activity in the field was, however, triggered by the search for new MR systems as well as half-metallic compounds.

An interesting question concerns the valence states of Fe and Mo. In the early ^{57}Fe Mössbauer study by Nakagawa, the spectra were interpreted as high-spin ($S=5/2$)Fe^{3+}, with a small reservation towards the possibility of high-spin ($S=2$)Fe^{2+}.[4] Consequently, Mo was assigned to the 5+ valence state, the spin of which is 1/2. This opinion was advocated by more recent reports as well.[1,5,6] Kobayashi *et al.* claimed that the coupling between Fe^{3+} and Mo^{5+} is ferrimagnetic, leading to a magnetic moment of $4\mu_B$ per formula unit.[1] It is noteworthy that the less likely ferromagnetic Fe^{2+}Mo^{6+} configuration also yields $4\mu_B$ per formula unit, so magnetization measurements alone cannot distinguish the Fe^{3+}Mo^{5+} configuration from the Fe^{2+}Mo^{6+} configuration. At 4.2 K the experimentally observed magnetization value was only $3.1\mu_B$ per formula unit.[1,6] This discrepancy is probably due to a slight ($\sim$10%) disorder between the Fe and Mo atoms.[2,7] Results from recent neutron diffraction experiments show that the spin on the Fe site is $4.1\pm0.1\mu_B$, while that on the Mo site is zero within the same statistical error.[6] The authors explained this by claiming that the antiferromagnetically coupled electron of the Mo^{5+} ion is itinerant and gives no local magnetization on the Mo site. Instead, it serves to decrease the net spin on the Fe site from 5/2 to 2.

In a recent work on the oxygen-deficient BaSmFe$_2$O$_{5+u}$ double-perovskite system a Verwey-type mixed-valence or valence-fluctuation state, formally expressed as Fe$^{2.5+}$, was observed.[8] In samples with a reduced oxygen content $u\approx0$, equal amounts of Fe atoms adopt valence states of 3+ and 2+ on a single lattice site. ^{57}Fe Mössbauer spectra recorded at room temperature are, nevertheless, dominated by a single magnetic component which formally can be assigned to the valence state Fe$^{2.5+}$.[8] Upon cooling the samples below the Verwey-type transition temperature ($T_V\approx200$ K) charge separation occurs and expected amounts of divalent and trivalent iron are found in the Mössbauer spectra.[8] Furthermore, very recent measurements show that the BaSmFe$_2$O$_{5+u}$ system also exhibits MR effects.[9] In the following, we will present evidence for the presence of the Fe$^{2.5+}$ valence-fluctuation state in Sr$_2$FeMoO$_{6-w}$.

The preparation of the Sr$_2$FeMoO$_{6-w}$ samples is reported elsewhere.[10] In brief, an encapsulation technique using an Fe getter and SrCO$_3$, Fe$_2$O$_3$, and MoO$_3$ as starting materials was employed. Coulometric titrations were carried out for establishing the oxygen content. Resistivity measurements under an applied field of 0–7 T were carried out in the temperature range of 5–300 K. The ^{57}Fe Mössbauer spectra of the sample were recorded at 5, 77, and 300 K in transmission geometry. The absorber was made by spreading the sample material mixed with varnish evenly on an Al foil. The thickness of the sample material (expressed in mass per area) was approximately 20 mg/cm^2. A linear Doppler velocity sweeping from -15 to $+15$ mm/s was used. An Amersham ^{57}Co:Rh (20mCi, December 1998) source was used for producing the Mössbauer γ quanta, during the time interval of September to October 1999. The spectra exhibiting magnetic splitting were fitted with the full Hamiltonian of combined electric and magnetic interactions. The following hyperfine parameters were included in the fit: the internal magnetic field experienced by the Fe nucleus (B), the chemical isomer shift relative to α-Fe (δ), the quadrupole coupling constant (eQV_{zz}), the resonance linewidth (Γ), and the relative intensity of the components (I). The following conditions and constraints were applied: (i) For each component a

[a]Permanent address: Department of Physics, Åbo Akademi, FIN-20500 Turku, Finland.
[b]Permanent address: Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, FIN-02015 Espoo, Finland.
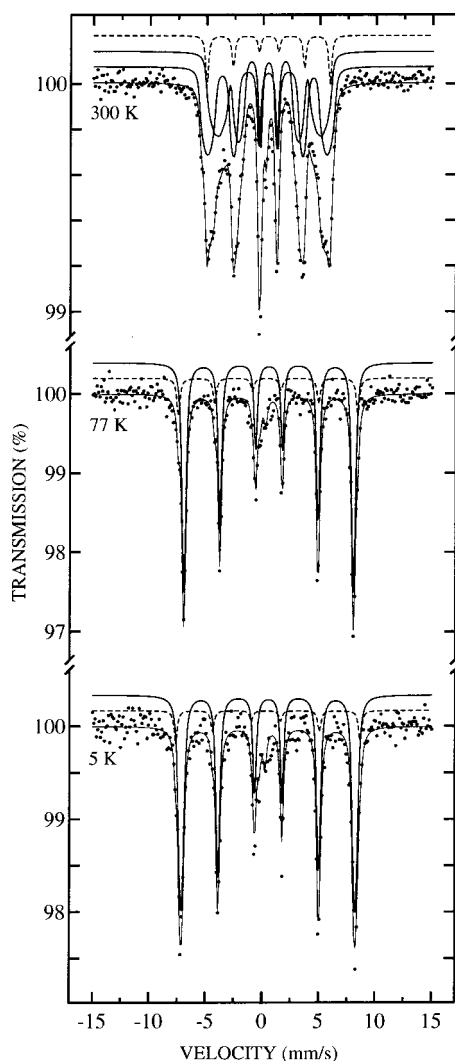[c]Author to whom correspondence should be addressed; electronic mail: yamauchi@materia.titech.ac.jp

FIG. 1. Mössbauer spectra of the Sr_2FeMoO_{6-w} sample obtained at indicated temperatures. Component 1 (along with the satellite at 300 K) and component 2 are drawn using full and dashed lines, respectively.

certain variation in the parameter B was allowed in order to simulate the fact that the internal fields have a certain spread due to, e.g., disorder between Fe and Mo atoms (at next-neighbor sites), temperature effects, etc. A Gaussian distribution was assumed and its width (ΔB) was introduced as a fit parameter. (ii) The asymmetry parameter η and the angle θ between the direction of the magnetic and the electric quantization axes were set equal to zero. (iii) All components were constrained to have equal line widths Γ. (iv) A small asymmetric quadrupole component, originating from traces of iron in the Be detector window and in the Al foil was kept fixed during the fits. These impurity defects cover less than $\sim 2\%$ of the spectral intensity obtained in the measurements.

The phase purity of the sample was confirmed by x-ray

diffraction. The structure was best described by the cubic $Fm3m$ symmetry.[10] The oxygen content of the sample was 6.00(2) atoms per formula unit according to the coulometric titrations,[10] thus effectively ruling out the possibility of oxygen vacancies in the following treatment. The resistivity measurements indicated a negative magnetoresistance of 8% at 300 K and 7 T, in accordance with the findings of Ref. 1. In Fig. 1, the spectra recorded from the Sr_2FeMoO_{6-w} sample at 300, 77, and 5 K are presented. The 300 K spectrum is basically identical to the one presented in Ref. 4. The 5 and 77 K spectra are well resolved and adequately fitted using two spectral components. The more intense component is denoted component 1 and the less intense one component 2. At 300 K the large and slightly asymmetric broadening of component 1 is accounted for by introducing a satellite component with a Gaussian distribution of the internal field value. In Table I, the hyperfine parameters obtained from the fit are given. As the satellite and component 1 are considered to have a common origin, the average values for the hyperfine parameters are presented for component 1. Due to the cubic crystal symmetry and the fact that there are no oxygen vacancies, all Fe and Mo atoms reside in regular six-coordinated oxygen polyhedra. The natural assignment for component 1, which covers 91% of the spectral intensity (at 5 K), is thus the regular Fe site. Component 2 is assigned to the disorder site, where Fe occupies the Mo site. Both components have rather small quadrupole coupling constants, as expected for a regular six coordination.

Using only the 300 K data assignment of the spin states is difficult. However, the internal field, the isomer shift, and the quadrupole coupling constant of component 1 are all practically identical to those reported for the $Fe^{2.5+}$ 300 K subspectrum of the $BaSmFe_2O_{5+u}$ system.[8] Also, by visual appearance the 300 K spectra of the Sr_2FeMoO_{6-w} sample and the reduced ($u \approx 0$)$BaSmFe_2O_5$ sample are essentially identical. The isomer shifts of both the components, S_1 and S_2 obtained from the fit of the Sr_2FeMoO_{6-w} spectrum, are very large (some 0.55 mm/s with respect to α-Fe), being at the very upper limit of what is expected for high-spin Fe^{3+}.[11] These facts are the first indications of the presence of the fluctuating $Fe^{2.5+}$ valence state.

The Curie temperature $T_C \approx 420$ K is rather high.[6] At 5 K the internal fields have thus reached their saturation values. The 47.6 T field of component 1 is too weak for a high-spin Fe^{3+} state. This is also a strong indication of a transfer of the Mo $4d^1$ electron towards the Fe site, decreasing its formal valence from 3+ towards 2.5+. Inside a regular octahedral polyhedron field values well above 50 T would be expected for high-spin Fe^{3+}.[12] Thus, the 50.5 T field of component 2 complies better with high-spin Fe^{3+}. As it is believed to originate from the disordered Fe atoms at the Mo site, it is

TABLE I. Hyperfine parameters of the Sr_2FeMoO_{6-w} sample.

T	I_1 (%)	I_2 (%)	B_1 (T)	B_2 (T)	δ_1 (mm/s)	δ_2 (mm/s)	eQV_{zz}^1 (mm/s)	eQV_{zz}^2 (mm/s)
300 K	93(4)[a]	7.4(8)	30.2(2)	33.73(9)	0.55(1)	0.57(1)	−0.03(6)	−0.08(4)
77 K	87(3)	13(1)	46.46(3)	49.2(1)	0.658(3)	0.52(2)	−0.03(1)	0.25(9)
5 K	91(3)	9(2)	47.63(4)	50.5(2)	0.663(4)	0.54(4)	−0.04(2)	0.4(2)

[a]Includes satellite intensity.

completely surrounded by Fe cations. Therefore, the transfer of the Mo $4d^1$ electron is in this case inhibited and the valence state remains at $3+$. Subtracting a typical second-order Doppler shift of 0.1 mm/s (upon decreasing the temperature from 300 to 5 K) from the isomer shift values, component 2 complies well with high-spin Fe^{3+}, whereas component 1 still remains at the upper boundary of what is expected for high-spin Fe^{3+}. Considering that the lower boundary of isomer shift for high-spin Fe^{2+} is about 0.78 mm/s,[11] and that typical field values are around 40 T, component 1 exhibits all essential features of a high-spin $Fe^{2.5+}$ valence-fluctuation state. The quadrupole coupling constants should be close to zero for both components in accordance with the symmetric oxygen coordinations. Component 2 has an eQV_{zz} value, which is slightly increased, but still well in accordance with coordination number six. It is noteworthy that in the reported cases of mixed-valence fluctuations the quadrupole coupling constant has been found to be zero, independent of the local symmetry.[8,13] This observation could explain why eQV_{zz} actually reaches zero for component 1, but not for component 2.

The magnetic moments obtained by neutron-diffraction measurements (Ref. 6) support the valence-fluctuation picture, because the spin in the $Fe^{2.5+}$ state is formally 2.25, which gives a net magnetic moment of $4.5\mu_B$ for Fe and a mere $0.5\mu_B$ for that of Mo. These values should not be taken too literally, rather we would like to emphasize that an antiferromagnetically coupled itinerant electron reducing the spin of the Fe site, should likewise reduce the valence state giving rise to the particular valence-fluctuation state observed in this system. Anyhow, by taking into account the Fe/Mo disorder on top of this, the experimental moments of $4\mu_B$ and $0\mu_B$ observed for the Fe and the Mo sites, respectively, seem appropriate. Contrary to the $BaSmFe_2O_{5+u}$ system, no transition to a charge-separated state was observed at temperatures above 5 K. Furthermore, as the resistivity and susceptibility data show smooth behavior down to 4.2 K, the itinerant electron causing the valence-state fluctuation would remain intact down to 4.2 K. As spin-polarized itinerant electrons are responsible for the giant MR effects observed in powder samples, or rather the half-metallic nature of the present system, it is conceivable that the valence-fluctuation state is yet another manifestation of the same phenomenon.

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