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The magnetic effects in Sr_2FeMoO_6 perovskite type compound obtained by soft chemistry

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Recently, a double perovskite oxide, Sr_2FeMoO_6, has been reported to show a very sharp magnetoresistance (*M*R) response at relatively small-applied fields and at high temperatures. The half-metallic state of this compound ensures a theoretical magnetic moment of 4 μ_B per formula unit. Ordering control is expected to be influenced by the synthesis route. In this regard, in this article, perovskite samples were obtained from the liquid phase, using oxalic acid as complexing agent. Application of a field above 0.08 T increases the zero-field-cooled (ZFC) magnetization. Below this field, for the ZFC-curves measured from 2 K up to 400 K, magnetization increases, reaching a peak at T_{cups}^{ZFC}, before decreasing gradually to a paramagnetic state. Saturation moment is relatively low (2.1-2.2 μ_B), probably due to anti-site defects, as suggested in the literature.

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1. Introduction

Double perovskite oxide, Sr_2FeMoO_6 (SFMO), has been reported to show a very sharp magnetoresistance (MR) response at relatively small-applied fields and at high temperatures [1]. The discovery of metallic ferrimagnetism in these materials has stimulated both fundamental and applied research. Subsequent extensive work on this compound has established that the tunneling of charge carriers across non-conducting barriers, where the application of a magnetic field enhances the tunneling probability, increasing the electrical conductivity significantly, mainly drives the magnetoresistance response. The peculiar properties have arisen from half-metallic density of states in the electronic structure of SFMO [1-3], implying a complete (100 %) spin polarization of the charge carriers. The up-spin band is gapped, corresponding to $3d^5$ spin-up electron localized in Fe^{3+} ions, whereas the conduction band is partially occupied by the $4d^1$ down-spin electrons of Mo^{5+} ions. The half-metallic state of this compound ensures a magnetic moment of 4 μ_B per f.u. Same was concluded on the basis of the ionic description. However, the half-metallic states, and consequently the magnetic moment, depend critically on the perfect ordering of the Fe and Mo sites alternating along three axes. The low saturation moment (3.1-3.2 μ_B) observed by several groups [1,2,4,5] was attributed to anti-site defects resulting from the partial disorder of Fe-Mo ions among the B/B' sublattices [2,5].

Recently, Raekers et al. [6] have shown by XPS studies, that in SFMO occurs a mixed valence state involving around 30 % Fe^{3+} - Mo^{5+} and 70 % Fe^{2+} - Mo^{6+} states.

Search for new routes or optimizing the current ones is expected to enhance the properties of the material towards theoretical values. Stoechiometry control vs. disorder and defects plays a major role and it is easy to understand that synthesis and processing of the material are important to enhance material quality. Considering that solid state reactions between component oxides mechanically mixed cannot assure the imposed condition, many researchers applied modern synthesis routes offering a better compositional control and providing reactive precursors [7]. Our effort is concentrated in the same direction and an oxalate complexing synthesis method is proposed in this article.

2. Experimental

A mixture of $SrCO_3$, $Fe_2(NO_3)_3{\cdot}4H_2O$ and $MoO_3{\cdot}H_2O$ (cation ratio 2Sr:Fe:Mo) in an acid solution of a complexion agent, in our case the oxalic acid ($C_2H_4O_2$), was precipitated through the etherification reaction with ethyl-glycol. The oxalic acid has the advantage of influencing the process in two ways: one is the reducing character of the acid itself and the other is the occurrence of two-hydroxyl groups able to bond the cations.

The precursor was then dried in the air at room temperature, and calcined up to 1200 °C, also in the air, to obtain the oxide powder.

The compacts obtained from the as-prepared powder were submitted to a thermal treatment in reducing atmosphere (5% H_2/Ar) for 2-4 hours in order to reduce the Mo^{6+} to $Mo^{5+}$and/or Fe^{3+} to Fe^{2+}. It is assumed that, during this heat treatment, electron hoping from Mo to Fe is induced, and this is probably responsible for the observed magnetoresistive effect.

The structure and phase purity of the sample were checked by X-ray diffraction (XRD) with Cu K_α radiation at room temperature performed on PANalytical/Phillips. The temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations $M_{ZFC}(T)$ and $M_{FC}(T)$, respectively, were measured using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2 – 400 K, and the magnetic range of 0 - 0.5 T. Magnetization loop M-H was measured at 5 K.

3. Results and discussion

Precursors were investigated by elemental chemical analysis and IR spectroscopy in order to see the species formed after the synthesis reaction.

IR spectroscopy (400 – 4000 cm^{-1}) on the precursors revealed the presence of characteristic vibrations for the carboxyl group (ν_{COO^-}), which indicates the presence of poly-nuclear oxalates of Fe and Mo.

The presence of weak vibrations in the 1400 cm^{-1} confirmed the presence of complex oxalates which decompose when heated, leading finally to oxides with the general formula $Sr_4[Fe_2Mo_2O_4]$. The experimental data showed that the major oxide specie with the formula 4SrO Fe_2O_3 $2MoO_3$ (40.64%Sr/12.94%Fe/22.26%Mo) is formed.

XRD revealed the formation of the double perovskite as major phase in the final product (Fig. 1). The X-ray pattern was fitted with the theoretical profile for the tetragonal I4/m structure. Lattice parameters a = 5.55 Å and c = 7.86 Å, and it is very close to the one reported in the literature a = 5.5686 Å and c = 7.8985 Å [8].

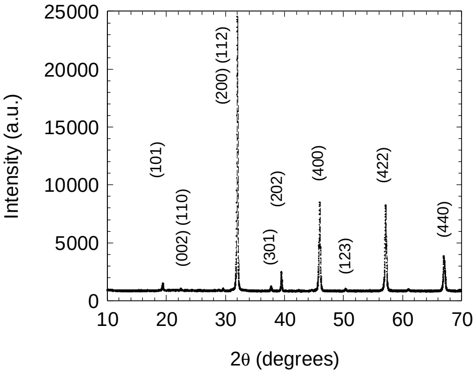

Fig.1. X-ray pattern for Sr_2FeMoO_6 sample.

Figs. 2 and 3 show representative M-T curves measured under different applied magnetic fields between 0.002 and 0.5 T. One can note the following features:

a) When applying a field above 0.08 T, ZFC magnetization (Fig. 2) decreases with temperature. Below this field, with the increase of temperature from 2 K a peak at T_{cusp}^{ZFC} is reached, followed by a gradual decrease toward a paramagnetic state. The values of the peak are given in Table 1.

Table 1. T_{cusp}^{ZFC} data determined from M_{ZFC} vs. T curves.

H (T)	T_{cusp}^{ZFC} (K)
0.002	344
0.006	337
0.01	328
0.03	268

b) All FC curves (Fig. 3) increase vs. field and show a strong tendency to saturate to T = 0 K over the whole range of the applied fields.

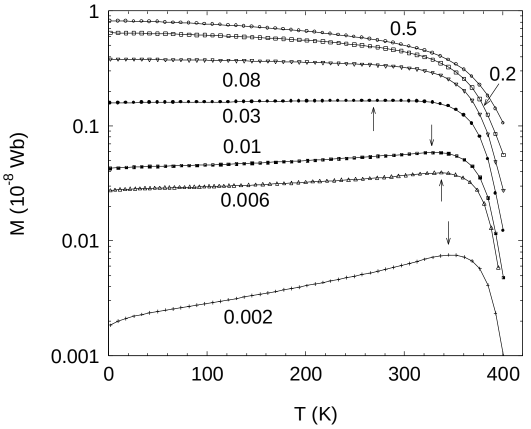

Fig. 2. Magnetization vs. temperature in different magnetic fields measured under ZFC condition. The arrows indicate T_{cusp}^{ZFC} values.

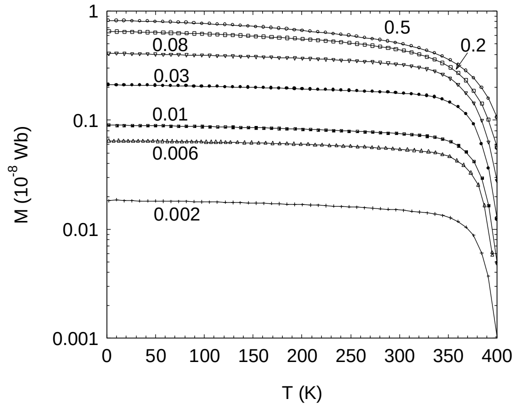

Fig. 3. Magnetization vs. temperature in different magnetic fields, measured under FC condition.

The ordering temperature T_c from a paramagnetic to a ferrimagnetic state is above 400 K, and above the working temperature limit of our equipment.

The above magnetic phenomena can be easily understood as the existence of two magnetic sublattices, one aligned with the applied field and the other antiparallel with the field.

The magnetization loop at 5 K is shown in Fig. 3. This measurement was performed from a ZFC condition, under an external field varying between – 2 and + 2 T. At this temperature, sample is characterized by a coercitive field μ_0H = 0.014 T. The magnetization rises dramatically at low field and tends to saturate at high field. Our extrapolated calculus up to 5 T shows only 2 % increase of the magnetization. The saturation magnetization at 5 K is ≥ 2.1 μ_B per formula unit. However, the observed total magnetic moment is smaller than the expected value. This variation can be attributed to the effect of anti-site disorder at the octahedral Fe, Mo cation sublattices [2, 8]. Our value is the same as on the literature [5,7].

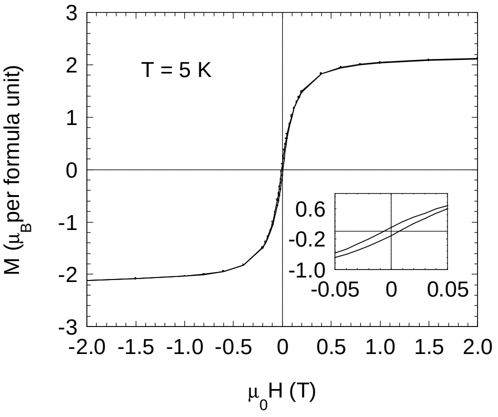

Fig. 4. The magnetization vs. applied magnetic field at 5 K. Inset shows a low field detail.

In a field-cooled measurement (FC) under small fields, as the temperature is decreased from T_c, the Fe sublattice orders ferromagnetically, creating a local field at the Mo site; at the same time, due to the negative *f-d* exchange interaction, the Mo sublattice tends to align antiparallel to such local field. However the antiparallel sublattice magnetization grows more slowly with decreasing temperature than the aligned one, and the T_{comp} (i.e the temperature below which a antiferromagnetic component might occur and decrease magnetization) is not reached for all applied fields. When the applied magnetic field is high enough, it over-comes the internal field produced by the Fe sublattice, and will predominate over the susceptibility of the Mo. The Mo ions remain parallel to the external field.

Indeed, during the ZFC process, the Fe magnetic domains are locked in random directions, giving rise to an antiferromagnetic canted state characteristic of these perovskite materials. When an external field of 0.002 T is applied at low temperature (e.g., 2 K), the total magnetization (M_{Fe} – M_{Mo}) takes a small positive value because the Mo moments are not large enough to overcome the local field. Since the measurement field is smaller than the coercivity (H_c = 0.014 T at 5 K), it is rather hard for the Fe domains to rotate at these temperatures. Then, with increase of temperature, due to the smaller coercivity above 5 K, the domains can gradually rotate to the external field direction ensuring that the total magnetization parallels the *H* direction. Meanwhile, the antiparallel sublattice magnetization grows more slowly with increasing temperature than the aligned one. Hence, a quick increase of magnetization from 2 to about 344 K can be noted. At higher temperatures, the magnetic ordering is restrained, reaching the paramagnetic state and decreasing afterwards. This effect decreases at higher applied field, thus that above 0.03 T the contribution of local magnetic ordering is suppressed by external field (Table 1).

Irreversibility between the $M_{ZFC}(T)$ and $M_{FC}(T)$ curves in the fields below 0.2 T is clearly seen close to T_C. The thermomagnetic irreversibility arises from magnetic anisotropy or is due to spin-glass-like behavior (mictomagnetic type behavior) as reported in many-order magnetic systems. In an attempt to compare to ordinary spin glass in validity of the De Almeida-Thouless line and Gabay – Toulouse line [10,11], we plotted the reduced temperature $\theta = T_{cusp}^{ZFC} / T_C$ vs. H and have found that θ scales with H as $\theta \propto 1-(a / T_C)\cdot H^n$, where a and n are constants. The result of n = 1.33 shows that from the magnetic point of view our samples are placed in Gabay - Toulouse (GT) vector model spin glass phase diagram [11] between these lines. The drop of the $M_{ZFC}(T)$ at lower temperature in H = 0.002 T seems to be the spin-freezing temperature (T_f = 50 K), i.e. the transition to ordinary spin glass behavior to lower temperatures.

4. Conclusions

Sr_2FeMoO_6 was obtained by a liquid phase synthesis route, using oxalic acid as complexing agent. The obtained properties are promising and further improvements are anticipated through the refinement of our synthesis method.

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