

Room-temperature magnetism in chemically oxygenated conducting oxide $\text{Sr}_2\text{FeCoO}_6$

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Abstract

Using chemical oxidation technique, we prepared a new half-metal $\text{Sr}_2\text{FeCoO}_6$. Mössbauer study has presented a simultaneous test of stability of the oxygen content in this material. Caused by the oxygen leak, the Mössbauer spectra were progressively changed in the sample kept at room temperature. The spectra were measured within 3 months alternately with and without field of 4 kOe of a permanent magnet. The strong magnetizing effect of such a moderate field is conceptually well explained by nanostructuring, assisted by the unexpected effect of the superparamagnetic fraction permanently increasing with the “leak-time”.

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1. Introduction

Several transparent conducting oxides can become ferromagnetic when doped with transition metal ions, which substitute a small fraction of ions of host elements in an oxide lattice. Origin of the magnetic exchange in these dilute magnetic semiconductors (DMS) is quite unusual, and remains yet unclear even if it commonly exhibits a resemblance to the exchange coupling in concentrated magnetic systems, such as double-exchange manganites and Fe-based half-metals of $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_2\text{FeCoO}_6$ [1].

On the other hand, thin films of magnetically ordered perovskites, such as SrFeO_3 , are expected to be relatively transparent in the major part of the visible light region of wavelengths, contrarily to the opaque thin films of high- T_c superconductors [2]. In addition, when Fe and Co are mixed in the same site of

the perovskite structure, the conductivity increases by orders of magnitude (see, e.g., Fig. 2 in Ref. [3]).

In the form of thin films, the fully oxygenated stoichiometric perovskite $\text{SrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ was first synthesized by Hayashi et al. [4], who have employed the pulsed laser deposition (PLD) of the perovskite onto LaAlO_3 substrates. They have achieved the full oxidation of the films using ozone blasting against the film surface at a typical PLD pressure of 10^{-2} Torr. The single-crystalline films with metallic conductivity have contained iron with only the “4+” oxidation state [4]. When no ozone blow was applied to the growing film in previous work [5], the films were semiconducting. The powders of $\text{SrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ were synthesized by loading their precursors at a pressure of several GPa with the oxidation agent KClO_3 [6] and electrochemically [7]. The oxygen-deficient powders of $\text{SrCo}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ synthesized under a moderate oxygen pressure of around 10 MPa also show half-metallic conductivity with narrower range of magnetic order at low temperature only [3,8]. Half-metallic ferromagnets exhibit metallic behavior for one spin polarization and insulating for the other. Near Curie point (T_c) some of them show the intrinsic magnetic nanostructuring, observed via maximum

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near T_c in the resistivity curves $\rho(T)$ [9]. External magnetic fields suppress the maximum thus producing the effect of magnetoresistance. In ferromagnetic manganites, this suppression is the most pronounced, caused apparently by the mechanisms of field-induced growing the magnetic domains and swelling the magnetically ordered conducting stripes.

Through the electron–phonon interactions the transition at T_c manifests itself in vibrational density of states (DOS) $g(E)$ as a softening of several phonon branches and of the whole DOS [8]. Since the wide range of oxygen deficiencies is the intrinsic property of these perovskites, both the oxygen-saturated $\text{SrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ powders [6,7] and their oxygen-deficient counterparts [3,8] are the subject of stability check. When performing the previous work [8], we observed that the sample properties were gradually changing, so that the results of several subsequent property measurements differed one from another.

In this work, we have performed the unequivocal tests of oxygen stability in the samples, starting to train the samples from the maximum oxygen content in the dense pellets of $\text{SrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ sintered carefully using the ceramic technology. Using the method of chemical oxidation [10,11] we have prepared the half-metal $\text{Sr}_2\text{CoFeO}_6$ having its T_c above room temperature. A simultaneous test of stability of the oxygen content in this material has been studied by Mössbauer spectrometry, and phonon DOS of $\text{Sr}_2\text{CoFeO}_6$ and the related compounds, $\text{SrCo}_{0.3}\text{Fe}_{0.2}\text{Nb}_{0.5}\text{O}_{3-\delta}$ and $\text{SrCo}_{0.5}\text{Fe}_{0.2}\text{Nb}_{0.3}\text{O}_{3-\delta}$, are presented here.

2. Experimental

The samples were synthesized by the routine ceramic method from the corresponding metal oxides and carbonates. Stoichiometric mixture of initial reagents was homogenized in planetary ball mill AGO-2 and calcinated at 900 °C (6 h), then pressed in pellets and annealed in air at 1200 °C (6 h). Chemical

oxidation was achieved by alkaline hypobromite solution as described previously [10]. Phase analysis was carried out by means of X-ray diffraction; oxygen stoichiometry was determined by iodometric titration.

Two series of polycrystalline samples of $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ investigated were made from the pellets enriched in ^{57}Fe (sample 1) and unenriched (sample 2), respectively. In both series, we measured the Mössbauer spectra without and with the external field from a permanent magnet of ca. 4 kOe, applied parallel to the γ -propagation direction. The enriched samples were also used for measurements of nuclear resonant scattering (NRS) using the techniques described previously [8,12]. The enrichment was 20% in the enriched series of $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ and also in the oxygen-deficient phases of $\text{SrCo}_{0.3}\text{Fe}_{0.2}\text{Nb}_{0.5}\text{O}_{3-\delta}$ and $\text{SrCo}_{0.5}\text{Fe}_{0.2}\text{Nb}_{0.3}\text{O}_{3-\delta}$ synthesized by the ordinary ceramic method in air. Nuclear inelastic scattering (NIS) of X-rays was studied in both oxygen-saturated and oxygen-deficient series of samples at the beam line BL11XU of the Spring8 synchrotron with the resolution in the frequency of 0.6 THz. Inelastic scattering spectra of air-synthesized samples were obtained also in the same batch as reference specimens from the family of brownmillerite and perovskite-related compounds, which reproduced well the vibrational DOS spectra published previously in brownmillerites $\text{CaFeO}_{2.5}$, $\text{CaSrFeO}_{2.5}$ [13,14] and oxygen-deficient perovskites $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ [1,8].

3. Results and discussion

Room-temperature Mössbauer spectra of $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ are shown in Fig. 1 for two samples. The sample 1 was grounded from a larger size unenriched pellet, and the sample 2 was made from the small-enriched pellet. The time is elapsing in Fig. 1 from left to right. The effect of oxygen leaking is observed to be stronger from the enriched pellet. The abundance of magnetically ordered ^{57}Fe species in dense pellet was twice larger at the

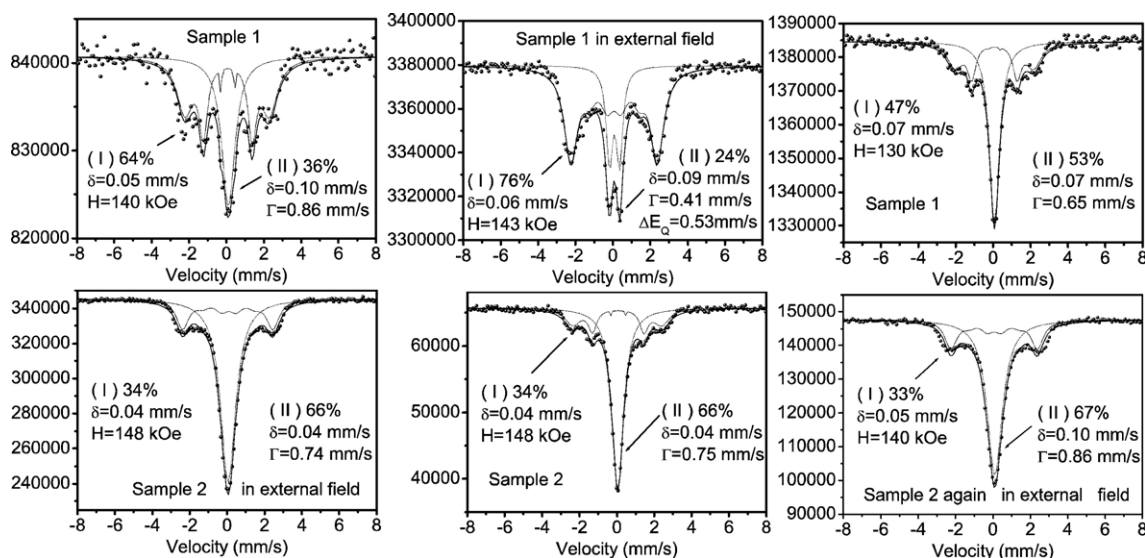


Fig. 1. Mössbauer spectra in oxygen-leaking samples 1 and 2 measured alternatively with and without external field using the following sequences: zero-field $\rightarrow$ 4 kOe $\rightarrow$ zero-field (sample 1) and 4 kOe $\rightarrow$ zero-field $\rightarrow$ 4 kOe (sample 2). The time increases from left to right in both rows of spectra.

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