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Structural and magnetic properties of $\text{RSr}_2\text{Fe}_3\text{O}_9$ ($\text{R}=\text{La}$, Y , Pr , and Gd)

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We have investigated the $\text{RSr}_2\text{Fe}_3\text{O}_9$ ($\text{R}=\text{La}$, Y , Pr , and Gd) materials by several experimental techniques, including x-ray and neutron diffraction, magnetic susceptibility, and Mossbauer spectroscopy measurements. All materials studied are single phase and crystallize in the hexagonal perovskite structure. Magnetic susceptibility studies reveal that, for $\text{R}=\text{La}$ and Pr , the Fe ions order antiferromagnetically at about $T_N=190$ K. Short range magnetic correlations are observed up to 250 K. For $\text{R}=\text{La}$ and Pr , ^{57}Fe Mossbauer studies reveal two inequivalent magnetic sextets below 190 K, with the area ratio 2:1. Above T_N , one singlet is observed with an isomer shift value typical to Fe^{4+} . For $\text{R}=\text{Y}$ and Gd , the magnetization curves do not lend themselves to easy determination of the magnetic transition due to an extra magnetic phase which exists up to 350 K. This phase is a result of deficiency of oxygen. The ^{57}Fe Mossbauer spectra at 300 K indicate two superimposed singlet lines, and contain a small magnetic sextet. There is no indication that the R sublattice in $\text{RSr}_2\text{Fe}_3\text{O}_9$ ($\text{R}=\text{Pr}$ and Gd) orders magnetically down to 1.5 K. © 1998 American Institute of Physics. [S0021-8979(98)49511-2]

I. INTRODUCTION

Discovery of high T_c superconductivity (HTSc), above 90 K in (rare earth) R based oxygen deficient perovskite cuprates $\text{RBa}_2\text{Cu}_3\text{O}_7$ ($\text{R}:\text{123}$) has provoked considerable interest in superconductivity and magnetism of various R based perovskites.^{1,2} In principle, R:123 type compounds can be obtained with Ba replaced by Sr and Cu replaced by Fe.^{3,4} Fe based oxides ($\text{RBa}_2\text{Fe}_3\text{O}_8$ and $\text{RSr}_2\text{Fe}_3\text{O}_8$) are not superconducting.³⁻⁵ There are reports of structural magnetic and thermal measurements on some members of the series $\text{RBa}_2\text{Fe}_3\text{O}_8$ (RBFO).³⁻⁷ Also a unique behavior of $\text{PrBa}_2\text{Fe}_3\text{O}_8$ (PBFO), in terms of magnetic and thermal properties was observed in comparison to other R counter parts of the same formula.^{8,9} RBFO compounds are more or less widely explored until now.³⁻⁹ On the other hand for $\text{RSr}_2\text{Fe}_3\text{O}_9$ (RSFO), while the structural details are available for most of R members,¹⁰ detailed magnetic measurements were reported recently only for $\text{LaSr}_2\text{Fe}_3\text{O}_9$ (LSFO).¹¹

In present the article we report details of the structural and magnetic properties of RSFO compounds with $\text{R}=\text{Y}$, La , Pr , and Gd . Details of neutron diffraction, magnetic measurements, and Mossbauer spectroscopy are to be presented.

II. EXPERIMENT

The samples of RSFO with $\text{R}=\text{Y}$, La , Pr , and Gd were synthesized through a solid state reaction route with ingredients of Y_2O_3 , La_2O_3 , Pr_6O_{11} , Gd_2O_3 , SrCO_3 , and Fe_3O_4 . The samples were calcined and reground several times at temperatures of 950, 1000, 1050, 1100, 1150, 1200, 1250, 1300, 1350, and 1400 °C, for 24 h at each temperature, to ensure the formation of single phase compounds. The samples were further annealed at 1000 °C for 48 h in flowing oxygen and were subsequently cooled to room temperature in the same gas atmosphere over a span of 10 h. Neutron diffraction patterns were obtained at room temperature on the powder diffractometer at the Missouri University Research Reactor Centre, with neutrons of wavelength 1.7675 Å. The dc magnetic measurements on solid ceramic pieces in the range of 2–300 K were performed in a commercial (Quantum Design) superconducting quantum interface device (SQUID) magnetometer. The magnetization was measured by two different procedures. (a) The sample was zero field cooled (ZFC) to 5 K, a field was applied and the magnetization was measured as a function of temperature. (b) The sample was field cooled (FC) from above 300 to 5 K and the magnetization was measured. The Mossbauer spectroscopic studies (MS) were carried out using a conventional

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FIG. 1. Observed and fitted neutron diffraction patterns for $\text{LaSr}_2\text{Fe}_3\text{O}_9$ and $\text{PrSr}_2\text{Fe}_3\text{O}_9$ samples, shown one over the other, and taken at room temperature.

constant acceleration spectrometer. The ^{57}Fe MS were measured with a 50 mCi $^{57}\text{Co}:\text{Rh}$ source and the isomer shift (IS) are reported with respect to metallic Fe.

III. RESULTS AND DISCUSSION

A. Neutron diffraction

Figure 1, depicts the observed and fitted neutron diffraction patterns for RSFO samples with $\text{R}=\text{La}$ and Pr . As evident from this figure, the samples are single phase with no impurity lines in the neutron patterns. All the samples of series RSFO with $\text{R}=\text{Y}$, La , Pr , and Gd crystallize in the Rhombohedral structure ($a=b\neq c$, $\alpha=90^\circ$, $\beta=90^\circ$, and $\gamma=120^\circ$) with space group $R3c$. Earlier a cubic structure was proposed for the LSFO compound,^{4,5} but later it was observed that nearly all R with formula RSFO are better fitted in a hexagonal structure.¹⁰ The same is true for our samples also, where we observed a very good fit to the observed patterns with a $R3c$ hexagonal structure, see Fig. 1. The a , b , and c lattice parameters for various samples of RSFO series are as follows:

$\text{YSr}_2\text{Fe}_3\text{O}_9$

$$a=b=5.4664(7) \text{ \AA}, \quad c=13.3793(34) \text{ \AA},$$

$\text{LaSr}_2\text{Fe}_3\text{O}_9$

$$a=b=5.4883(7) \text{ \AA}, \quad c=13.4331(31) \text{ \AA},$$

$\text{PrSr}_2\text{Fe}_3\text{O}_9$

$$a=b=5.476\,01(15) \text{ \AA}, \quad c=13.3819(7) \text{ \AA},$$

and $\text{GdSr}_2\text{Fe}_3\text{O}_9$

FIG. 2. Temperature dependence of the susceptibility for $\text{PrSr}_2\text{Fe}_3\text{O}_9$ measured at 20 Oe, and the ZFC branch in inset. Note that the ZFC and FC branches merge at 260 K.

$$a=b=5.4668(9) \text{ \AA}, \quad c=13.3798(19) \text{ \AA}.$$

Our values of a , b , and c -lattice parameters for various samples, studied presently are comparable to those reported earlier.¹⁰ These values of lattice parameters also follow the ionic radius difference of the Y, La, Pr, and Gd. Lowest ionic size Y and Gd, are followed by relatively bigger ions La and Pr with increasing c -lattice parameters.

B. Magnetic behavior

The ZFC and FC magnetic susceptibility, measured at 20 Oe of $\text{PrSr}_2\text{Fe}_3\text{O}_9$ (PSFO) is shown in Fig. 2. Generally speaking, in both branches, only one distinct anomaly is observed. In analogy to $\text{PrBa}_2\text{Cu}_3\text{O}_7$,¹² it is possible that the Pr sublattice is magnetically ordered at low temperatures, but this ordering is not visible in the curves. We tend to believe that the anomalies in these branches are related to the Fe sites. The Neel temperature, $T_N(\text{Fe})$ is 195(1) K and is defined as the peak in the ZFC branch (Fig. 2 inset), which is above the sharp decrease position of the FC branch. Within the limit of uncertainty the same $T_N(\text{Fe})$ is obtained for La containing compound. It appears that T_N of Fe is about 200 K for all R, apparently independent of whether the trivalent R ions are magnetic (Pr, Fe) or not (Y, La). It is worth mentioning here that in RBFO compounds, the PBFO showed a unique behavior in terms of Fe ordering temperature.^{8,9} Particularly Fe moment orders around 700 K for all studied RBFO compounds, except PBFO, for which the same happens at around 290 K. The nearly linear (at high applied field) field dependence of the magnetization at 5 K (not shown), suggests that Fe sublattice order antiferromagnetically (AFM). The irreversibility probably arises from this AFM alignment of the Fe sublattice. It is assumed that in the FC process the external field causes the spins to cant slightly out of their original direction. This canting abruptly aligns a component of the moments with the direction of the field, and the FC branch is obtained. The effect of field strength on the irreversibility is significant. At low applied fields, the

FIG. 3. Mossbauer spectra of $\text{PrSr}_2\text{Fe}_3\text{O}_9$ in the paramagnetic state (210 K) and below $T_N(\text{Fe})$. The solid curves are theoretical least square fits in terms of 2 subspectra corresponding to inequivalent Fe sites.

field dependence of the magnetization is not linear, and the fact that the ZFC and FC curves merge at 260 K [above $T_N(\text{Fe})$], indicated the existence of an internal magnetic field at low temperatures, which vanishes at 260 K. The magnetic results, shown in Fig. 2, confirm our Mossbauer (MS) studies, which are displayed and discussed in the next section.

C. Mossbauer spectroscopy

Mossbauer spectrum of ^{57}Fe in $\text{PrSr}_2\text{Fe}_3\text{O}_9$ (PSFO) at 210 K [above $T_N(\text{Fe})$] is shown in Fig. 3. The main information obtained from visual and computer analysis is the presence of two subspectra corresponding to inequivalent Fe sites, which are immediately identified from their hyperfine parameters: the isomer shift (IS) and quadrupole splitting ($\Delta = 1/4e^2qQ$) values, with a common line width of 0.40(2) mm/s. The *dominant* line which accounts for 66% of the spectra area, has a small IS = -0.11 mm/s and a Δ of 0.06(1) mm/s and can be assigned as Fe^{4+} in the low spin state. Both, the IS = 0.17 and Δ = 0.07 mm/s of the *minor* doublet (33%), are typical to Fe^{3+} . For R=La, the MS measured at various temperatures (not shown) are very similar to the spectra shown in Fig. 3, proving the Pr ions are trivalent.

In fitting the experimental parameters below $T_N(\text{Fe})$, the iron in $\text{PrSr}_2\text{Fe}_3\text{O}_9$ (and for R=La), is composed of *predomi-*

nantly Fe^{3+} (66% at 4.2 K), Fe^{5+} (33% at 4.2 K), and an increasing fraction with temperature of Fe^{4+} (zero at 4.2 K). The 4.2 K spectrum (Fig. 3) is composed of two magnetic subspectra with IS = 0.37 and -0.03, an effective magnetic hyperfine field: H_{eff} = 469(3) and 269(2) kOe (the effective quadrupole splitting is zero for both sites), corresponding to Fe^{3+} and Fe^{6+} , respectively. These hyperfine parameters are consistent with this assignment. The spectrum at 90 K (Fig. 3) is fitted in the same manner. It thus assumed, that the nonmagnetic Fe^{4+} ions fraction increases with temperature and dilutes the magnetic Fe^{3+} and Fe^{5+} ions. At $T_N(\text{Fe})$, (the Fe^{4+} fraction becomes 66%) the magnetic order disappears.

IV. CONCLUSIONS

In conclusion we assume below $T_N(\text{Fe})$, the presence of Fe^{5+} (33% at 4.2 K, lowest IS and small H_{eff}) and Fe^{3+} (66% at 4.2 K, highest IS and large H_{eff}), and Fe^{4+} (0% at 4.2 K, intermediate IS and no H_{eff}). Whereas, at high temperatures [above $T_N(\text{Fe})$], most of the Fe ions are in non-magnetic Fe^{4+} state. The valance fluctuations occur only as a single electron process: $\text{Fe}^{5+} \rightarrow \text{Fe}^{4+}$ and $\text{Fe}^{3+} \rightarrow \text{Fe}^{4+}$.

In summary all the samples of series $\text{RSr}_2\text{Fe}_3\text{O}_9$ with R=Y, La, Pr, and Gd crystallize in hexagonal $R3c$ structure. Also their magnetic properties are very similar to each other. $\text{PrSr}_2\text{Fe}_3\text{O}_9$ behaves magnetically in a similar way as other $\text{RSr}_2\text{Fe}_3\text{O}_9$ compounds, unlike the case of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ and $\text{PrBa}_2\text{Fe}_3\text{O}_8$, which are reported to have unique behavior.^{8,9,12}

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