Mössbauer spectroscopy as a probe of magnetic states in La$_{0.5}$Ca$_{0.5}$FeO$_3$–δ perovskite

Ya-qiong Liang*, Nai-li Di, Zhao-hua Cheng

State Key Laboratory of Magnetism and Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

Received 28 October 2005; received in revised form 6 February 2006
Available online 10 March 2006

Abstract

Charge disproportionation in La$_{0.5}$Ca$_{0.5}$FeO$_3$–δ perovskite has been detected by zero-field Mössbauer spectra from 20 K to room temperature. On the basis of the parameters of center shifts and hyperfine fields, Mössbauer spectra identified that the iron ionic states are Fe$^{3+}$ and Fe$^{5+}$ below 150 K, Fe$^{3+}$, Fe$^{4+}$ and Fe$^{5+}$ in the intermediate temperature region, as well as Fe$^{3+}$ and Fe$^{4+}$ above 220 K. At low temperatures, the system exhibits a cluster-glass-like state resulting from competition between antiferromagnetic interaction of Fe$^{3+}$–Fe$^{3+}$ and ferromagnetic interaction of Fe$^{3+}$–Fe$^{5+}$.

© 2006 Elsevier B.V. All rights reserved.

PACS: 75.10.Nr; 82.30.Hk; 76.80.+y

Keywords: Cluster glass; Charge disproportionation; Mössbauer spectroscopy

1. Introduction

Iron perovskite compounds containing Fe$^{4+}$ ions have attracted much attention due to the unique character—charge disproportionation (CD). CD was first reported in CaFeO$_3$ below the charge disproportionation temperature ($T_{CD}$) 290 K by Takano et al. [1]. This character describes that the Fe$^{4+}$ ions could take discrete charge states as Fe$^{3+}$ and Fe$^{5+}$ (2Fe$^{4+}$→Fe$^{3+}$ + Fe$^{5+}$) depending on the temperature. The distribution of various valence iron ions and the interaction among them, before and after CD, can induce many interesting physical phenomenon, such as structural change, charge ordering, magnetic ordering and metal-insulation transition [2,3]. Mössbauer spectroscopy is a useful technique to study the magnetic properties. Therefore, it can clearly detect CD in the perovskites and related oxides containing Fe$^{4+}$ ions, such as Sr$_3$Fe$_2$O$_7$ [4] and Sr$_2$La$_{1/3}$FeO$_3$ [5]. Much valuable information regarding the atomic environment and magnetic interaction before and after CD transition can be deduced through the hyperfine parameters obtained from Mössbauer spectroscopy, i.e. center shift (CS), hyperfine magnetic field ($H_{hf}$), quadruple splitting ($QS$), area ratio of various sublattices, etc. Mössbauer spectroscopy for stoichiometric La$_{1-x}$Ca$_x$FeO$_3$–δ has been introduced in many papers [6–8]. These earlier researches focused on detecting Fe$^{3+}$ and Fe$^{5+}$ ions below $T_{CD}$ but rarely studying the complex magnetic properties arising from the interaction among the various iron ions. Thus we put our interests on the magnetic properties of La$_{1-x}$Ca$_x$FeO$_3$–δ originating from the competition between the ferromagnetic (FM) interaction in Fe$^{3+}$–Fe$^{5+}$ and antiferromagnetic (AFM) interaction in Fe$^{3+}$–Fe$^{3+}$ [9]. In this work, we selected the atomic scale $x = 0.5$ to get the maximum content of Fe$^{4+}$ ions [10] in order to obtain the maximum ferromagnetic interaction in the experiment. Below $T_{CD}$, a cluster-glass-like behavior induced by CD transition has been identified by the magnetization and Mössbauer spectroscopy.

2. Experimental details

La$_{0.5}$Ca$_{0.5}$FeO$_3$–δ polycrystalline powders were prepared by the traditional solid-state reaction method [7]. X-ray
diffraction (XRD) pattern reveals that the sample is single phase with an orthorhombically distorted perovskite structure (Pbmm space group). Magnetization measurements were performed on a commercial superconducting quantum interference device (SQUID) magnetometer. $^{57}$Fe Mössbauer spectra from 20 K to room temperature were recorded with a Wissel system constant acceleration Mössbauer spectroscopy system with a $^{57}$Co (Rh) source. A CCS-850 optical exchange helium gas closed cycle refrigerator was employed to provide variable temperatures from 20 K to room temperature. The values of CS given here are relative to the room temperature value of z-Fe.

3. Results

3.1. Magnetization measurements

Temperature dependences of zero-field-cooled (ZFC) and field-cooled (FC) DC magnetization for La$_{0.5}$Ca$_{0.5}$FeO$_3$ were measured in applied field of 1 kOe and illustrated in the main plot of Fig. 1. With decreasing temperature, ZFC magnetization ($M_{ZFC}$) exhibits a peak at 175 K ($T_P$) followed by a sudden decrease to a minimum. FC magnetization ($M_{FC}$) has a divergence with $M_{ZFC}$. It is the most intriguing feature in the main plot of Fig. 1. When $T_P < T < 300$ K, a kink in $M_{FC}$ and a smaller divergence between $M_{ZFC}$ and $M_{FC}$ are attributed to a very short-range ordering effect. It can be verified by the linear magnetization curve at 235 K (see the inset of Fig. 1), which indicates no FM component in the La$_{0.5}$Ca$_{0.5}$FeO$_3$ [11]. When $T < T_P$, a sharp increase in $M_{FC}$ indicates that some FM clusters exist. The linear magnetization curve at 100 and 150 K, seen the inset of Fig. 1, shows AFM component is dominant for La$_{0.5}$Ca$_{0.5}$FeO$_3$ in this temperature region. Thus, the larger divergence between $M_{ZFC}$ and $M_{FC}$ may suggest a magnetic glassy behavior.

![Fig. 1. Temperature dependence of magnetization for La$_{0.5}$Ca$_{0.5}$FeO$_3$ under applied field of 1 kOe in the zero-field-cooling and field-cooling process, respectively. The inset figure is the magnetization curves at 100, 150 and 235 K, respectively.](image)

3.2. Mössbauer spectroscopy measurements

In order to get the detailed information regarding the nature of glass behavior, the charge states and local environments of Fe nuclei, we carried out the zero-field Mössbauer spectroscopy measurements for La$_{0.5}$Ca$_{0.5}$FeO$_3$ from 20 K to room temperature, as shown in Fig. 2. The points in the figure are the experimental spectra and the solid lines represent the curve-fitted results. According to the earlier work, the Mössbauer spectra at low temperatures ($T < T_P$) should be a superposition of at least two components, corresponding to Fe$^{3+}$ and Fe$^{5+}$ ions. Moreover, the Fe$^{3+}$ component may be decomposed into two subcomponents due to the appearance of Fe$^{5+}$ ions, i.e. without Fe$^{5+}$ (Fe(I)) and with at least one Fe$^{5+}$ (Fe(II)) as their neighborhood [6-8]. Thus, we adopted three magnetic hyperfine fields to obtain the best fitting for La$_{0.5}$Ca$_{0.5}$FeO$_3$, corresponding to the three Fe ions sites; a Fe$^{5+}$ site and two Fe$^{3+}$ sites. When $T = T_P$, the Mössbauer spectrum becomes very complex, which reflects La$_{0.5}$Ca$_{0.5}$FeO$_3$ lying in a magnetic transition. Such complex spectra agree well with the sudden change in $M_{ZFC}$. We adopted four magnetic splitting sextets coexisted with one paramagnetic doublet to fit the spectrum. With further increasing temperature, the concentration of paramagnetic component increases. It is noticeable that the paramagnetic and the magnetic splitting patterns were superimposed over a wide temperature range. At room temperature, Mössbauer spectrum exhibits only one typical paramagnetic singlet.

Moreover, the splitting lines in the Mössbauer spectra have become broad from 150 K. We all know that the broadening of line width can be qualitatively considered as indication of a magnetic transition. However, this temperature is not equal to the transition temperature $T_P$ obtained from magnetization. The small discrepancy between the observed transition temperatures by Mössbauer spectra and magnetization may be due to a systematic error in the two temperature control systems, but a more likely possibility is that the two techniques responded differently within the timescale of progresses occurring in the vicinity of the transition.

The hyperfine parameters of all the components, obtained from the best fitting results for these spectra of La$_{0.5}$Ca$_{0.5}$FeO$_3$, as a function of temperature are shown in Fig. 3, respectively.

When $T < T_P$, CS and $H_{hf}$ are found to be a constant for three iron sites, as shown in Figs. 3(a) and (b). Among the three magnetically split sextets, one sextet with CS of 0.01 mm/s and $H_{hf}$ of 267 kOe is assigned to be Fe$^{5+}$ ions. The other two sextets with CS of 0.40 mm/s are Fe$^{3+}$ (I) with $H_{hf}$ of 520 kOe and Fe$^{3+}$ (II) with $H_{hf}$ of 490 kOe. When $T = T_P$, the forth sextet with CS = 0.25 mm/s and $H_{hf}$ = 283 kOe represents the Fe$^{4+}$ ions and the paramagnetic doublet with CS = 0.20 mm/s shows Fe$^{4+}$ ions. The appearance of Fe$^{4+}$ ions is a signature about the frozen electrons.
Fig. 2. The Mössbauer spectra of La$_{0.5}$Ca$_{0.5}$FeO$_{3-d}$ ranging from 20 K to room temperature. The black dots are experimental data; the blue lines are Lorentzian best fitting results; other curved lines represent the subspectra of various iron site.

Fig. 3. Temperature variation of the hyperfine parameters of various iron sublattices for La$_{0.5}$Ca$_{0.5}$FeO$_{3-d}$. (a) center shift (CS), the experimental error is $\pm 0.06$ mm/s; (b) hyperfine field ($H_{hf}$), the experimental error is $\pm 9$ kOe; (c) quadrupole splitting shift ($QS$), typical error is $\pm 0.07$ mm/s; (d) area ratio ($A$), error is $\pm 7\%$, the value of Fe$^{3.5+}$ is evenly shared to the contribution of Fe$^{3+}$ and Fe$^{4+}$ at room temperature according to the detailed room temperature spectra.
which can hop freely among the different iron sites and CD began to melt.

The temperature dependence of $QS$ can provide important information on the magnetic phase transition. The values of $QS$ for each component are shown in Figs. 3(c). When $T < T_p$, these values are near zero within the experimental error and essentially independent of temperature, which means the average $QS$ over all the orientation of $H_{hf}$ relative to the principal axes of the electric field gradient is zero [12]. Thus $La_{0.5}Ca_{0.5}FeO_3$ is in a magnetically order state at low temperature. At $T = T_p$, there is a sudden jump in magnitude of $QS$ from 0.01 mm/s to 0.35 mm/s, which indicates a magnetic transition.

The Mössbauer absorption area ratio ($A$) for various iron components as a function of temperature is plotted in Figs. 3(d). For profound understanding of the CD transition, we composed the area of two Fe$^{3+}$ sits into one component at low temperature ($T < T_p$), and on average divided the area of Fe$^{3.5+}$ ions ($T > T_p$) into the area of Fe$^{3+}$ and Fe$^{4+}$ components. From this figure, only two components of Fe$^{3+}$ and Fe$^{5+}$ exist at low temperature. Fe$^{4+}$ component appears up to 150 K and agrees with the deformation point in $M_{ZFMC}$. On the other hand, Fe$^{4+}$ is a rather high valence so that it does lie in a metastable complex. Thus oxygen vacancies are easily formed to decrease the energy level and to produce additional Fe$^{3+}$ ions in the perovskite. In our $La_{0.5}Ca_{0.5}FeO_3$, the ideal absorption area ratio of Fe$^{5+}$ ions at 20 K should be 25% corresponding to the charge balance. However, the actual ratio of Fe$^{5+}$ ions at 20 K is about 22% within the experimental error, which indicates that oxygen vacancies compensate the charge balance in $La_{0.5}Ca_{0.5}FeO_3$. Therefore, the oxygen vacancy $\delta$ is roughly estimated to be 0.03.

At room temperature, Mössbauer spectra exhibits a typical paramagnetic singlet with $CS = 0.20$ mm/s (see Fig. 2), which is similar to that reported in the literature [6,8]. However, the paramagnetic line is obviously broad with line width $\sim$0.4 mm/s, which is three times of the natural line width 0.14 mm/s. The natural line width is obtained from our $\alpha$-Fe experimental result at room temperature. The strange paramagnetic line width may be accounted for a superposition of several inequivalent crystallography sites. Thus, we measured the room temperature Mössbauer spectroscopy for more detail (see Fig. 4). It shows a little asymmetry in terms of two singlets: one is $Fe^{3+}$ ions with $CS$~0.33 mm/s and area ratio $\sim$55%, the other is $Fe^{4+}$ ions with $CS$~0.14 mm/s and area ratio $\sim$45%.

4. Discussion and Conclusion

From the above magnetization measurements for $La_{0.5}Ca_{0.5}FeO_3$, we found two magnetic transitions. One is from paramagnetic phase to a short-range-order phase at 300 K and the other is from short-range-order phase to a glass phase at $T_p$, which can be mirrored in the Mössbauer spectroscopy. However, the Mössbauer spectra in the short-range-order phase are extremely complex. Thus we put our interests on the second phase transition. In our fitted Mössbauer spectra, all the hyperfine parameters take sharp change at $T_p$. According to the results of $CS$ and $H_{hf}$, Fe$^{3+}$ and Fe$^{5+}$ were detected at low temperature ($T < T_p$) and Fe$^{3+}$ and Fe$^{4+}$ appeared at high temperature ($T > T_p$). Thus the magnetic transition at $T_p$ is the CD transition of Fe$^{4+}$ ions.

According to the Goodenough’s theory [9], the super-exchange interaction between Fe$^{3+}$ and Fe$^{5+}$ is FM interaction, and the interaction between Fe$^{3+}$ and Fe$^{3+}$ is AFM one, which have been verified by the neutron diffraction in $La_{1/3}Sr_{2/3}FeO_3$ [13]. Therefore two interactions may exist in $La_{0.5}Ca_{0.5}FeO_3$ at low temperature. Actually, the FM and AFM components were detected by the magnetization measurements (shown in Fig. 1). To ensure the fraction of the FM phase, which is trapped in the AFM host, compared to the total magnetic volume, we also measured the residual low temperature magnetization (not shown here). After $La_{0.5}Ca_{0.5}FeO_3$ was cooled in the 50 kOe magnetic field, the measurement of magnetization ($M$) vs. measured field ($H$) at 5 K allows an estimation of the percentage of FM phase. A small FM coupling component against the predominant AFM exchange coupling one can be calculated through $M$ vs. $1/H$. The FM residual moment (at 1/$H$~0) can be compared with the theoretical value for a purely FM sample. We assume an ideally purely FM sample, in which the FM interaction is completely based on Fe$^{3+}$–Fe$^{5+}$ interaction. Therefore the theoretical atomic moment of Fe$^{3+}$ ion is $5\mu_B$ and that of Fe$^{3+}$ ion is $3\mu_B$. Thus we obtain $4\mu_B/Fe$ in the hypothetically purely FM iron perovskite. The compared result shows the FM phase in our $La_{0.5}Ca_{0.5}FeO_3$ is approximately at the percentage of 7%. Such coexistence and competition between FM and AFM interaction may
induce abundance physical phenomenon, i.e. glass behavior.

It is well known that the superexchange mechanism is involving the 3d electrons of transition-metal ions and the 2p orbits of oxygen ions. Thus oxygen ion plays a very important role in the magnetic ordering of perovskite. In our \( \text{La}_0.5\text{Ca}_0.5\text{FeO}_3 \), oxygen vacancies is only 0.03 but it is enough to destroy the long-range superexchange interaction chain, which is one factor of the formation of cluster. Further, iron ions with various valences have different electronic structures. Consequently, they have various ionic radii. When CD transition happened, the possible difference of octahedral size between \( \text{Fe}^{3+} \) and \( \text{Fe}^{5+} \) will bring about the local strain. To let the intrinsic energy reaches the lowest level, the local strain can be relaxed if some clusters take place. Thus in \( \text{La}_0.5\text{Ca}_0.5\text{FeO}_3 \) there are some FM clusters (\( \text{Fe}^{3+}–\text{Fe}^{5+} \)) randomly distributing among the AFM matrix (\( \text{Fe}^{3+}–\text{Fe}^{3+} \)), which cause the hyperfine field is randomly oriented related to the principle axis of electronic field gradient. Therefore we obtained QS near zero below \( T_P \).

At room temperature, the broad line width lets us to assume that \( \text{Fe}^{3+}–\text{Fe}^{4+} \), \( \text{Fe}^{3+}–\text{Fe}^{3+} \) and \( \text{Fe}^{4+}–\text{Fe}^{4+} \) paramagnetic clusters exist in \( \text{La}_0.5\text{Ca}_0.5\text{FeO}_{3–\delta} \). Actually, this formation process of magnetic cluster, rooting in the random distribution of the doped calcium and the oxygen vacancies, is thought to exist over the entire range of the measurement.

In summary, the present study on \( \text{La}_0.5\text{Ca}_0.5\text{FeO}_{3–\delta} \) demonstrates that CD transition can occur below 175 K, which has been detected by the Mössbauer spectroscopy. The divergence of the magnetization between in the ZFC process and in FC process shows CD transition induces a cluster-glass magnetic behavior in \( \text{La}_0.5\text{Ca}_0.5\text{FeO}_{3–\delta} \) at low temperature, which is originated from the competition between FM interaction (\( \text{Fe}^{3+}–\text{Fe}^{5+} \)) and AFM interaction (\( \text{Fe}^{3+}–\text{Fe}^{3+} \)). At room temperature, this system shows a cluster paramagnetic state. These paramagnetic clusters are made of \( \text{Fe}^{3+} \) and \( \text{Fe}^{4+} \) ions due to the disordered arrangement of \( \text{La}^{3+} \) and \( \text{Ca}^{2+} \) and oxygen vacancies.

**Acknowledgment**

This work was supported by the State Key Project of Fundamental Research and the National Natural Science Foundation of China. ZHC thanks the Alexander von Humboldt Foundation for financial support and the generous donation of Mössbauer equipments.

**Reference**