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An investigation of phase separation by magnetic force microscopy in $La_{0.45}Sr_{0.55}MnO_{3-\delta}$ ($\delta \approx 0.01$)*

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We have found phase separation in $La_{0.45}Sr_{0.55}MnO_{3-\delta}$ (LSMO) by means of electron spin resonance, magnetic force microscopy (MFM) and magnetic measurements. Ferromagnetic and antiferromagnetic phases can coexist at low temperatures, and ferromagnetic and paramagnetic phases coexist when the temperature lies between the Néel and Curie temperatures. The size and shape of the ferromagnetic phases (the minority phases) was first observed directly from MFM images. It is suggested that the phase separation in LSMO is not the charge segregation type, but an electroneutral type due perhaps to the nonuniform distribution of oxygen vacancies.

Keywords: ferromagnetic cluster, phase separation
PACC: 7560N, 7530K

1. Introduction

Hole-doped manganites Ln_{1-x} A_x MnO_3 (Ln= rare earth, A=alkaline earth) with a distorted perovskite structure demonstrate a rich variety of physical phenomena such as colossal magnetoresistance,[1−3] charge and orbital ordering,[4−6] and phase separation (PS).[7−17] It is worth noting that PS has invoked considerable interest recently. According to the double exchange model and other related models, PS between ferromagnetic (FM) and paramagnetic (PM) phases,[18] antiferromagnetic (AFM) and PM phases, as well as FM and AFM phases[7,19,20] have been proposed theoretically. In addition, the PS has been confirmed experimentally in half doped $La_{0.5}Ca_{0.5}MnO_3$ [9,12,21] and $Pr_{0.5}Ca_{0.5}MnO_3$,[13] which are located at the boundary between the competing FM and AFM ground states. Subsequent electron spin resonance (ESR),[11] nuclear magnetic resonance (NMR),[15,16] and Mössbauer[22] investigations indicated that PS occurs not only in $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$, but also in various compositions of these materials. Consequently, as an intrinsic feature of perovskite manganites with strongly correlated electrons, PS has been admitted gradually.

Two different types of PS occur possibly in manganites.[23,24] One is the charge segregation type and the other is the electroneutral type. For the former, the competition between the attractive double exchange tendencies among carriers and Coulomb coupling determines the size and shape of the minority phases. As a result, the size of the minority phase regions is expected to be very small, about the order of a nanometre, due to the extended Coulomb interaction. However, for the latter, the size is much larger than that of the former due to no Coulomb force. Thus, a direct observation of the size and shape of the minority phase in the PS system is very important for obtaining a deep insight into the nature of PS. However, one noteworthy fact is that the size and shape of the minority phase has not yet been provided directly up to now. In this paper, we report on some results of detailed investigations of $La_{0.45}Sr_{0.55}MnO_{3-\delta}$ (LSMO) by means of ESR, magnetic force microscopy (MFM), and magnetic measurements. We found the PS between the FM and PM phases, as well as between the FM and AFM phases in the LSMO. Moreover, we have directly observed the size and shape of the FM regions (the minority phase) using MFM. According to the

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MFM results, it is suggested that the PS in LSMO is not a charge segregation type, but an electroneutral type caused perhaps by a nonuniform distribution of oxygen vacancies.

2. Experiment

Polycrystalline samples of LSMO were prepared by the solid-state reaction processing. For comparison, the sample of $La_{0.67}Sr_{0.33}MnO_3$, which exhibits an optimal ferromagnetism,[25] was prepared at the same time. The well-mixed stoichiometric mixture of La_2O_3, $SrCO_3$ and $MnCO_3$ powders was calcined at 1000°C in air for 24h. The resulting powders were reground by high-energy ball milling in air for 4h. The as-obtained powders were pressed into pellets and sintered at 1300°C in air for 48h, then furnace-cooled to room temperature. The phase purity and crystal structure of the synthesized samples were examined by means of the powder x-ray diffraction, performed on a Rigaku D/Max 2500 X-ray diffractometer with a rotating anode and Cu $K\alpha$ radiation. Rietveld refinement results indicate that no secondary phases can be detected in the resolution of the x-ray diffraction pattern (see Fig.1). Redox titration indicated that the LSMO is slightly oxygen-poor ($\delta \approx 0.01$). The magnetization measurements were performed in a commercial SQUID magnetometer. The micromagnetic properties were investigated by ESR measurements carried out at 9.50GHz using a BRUKER-200D spectrometer. The MFM images were obtained using the Nanoscopy IIIa MFM at room temperature.

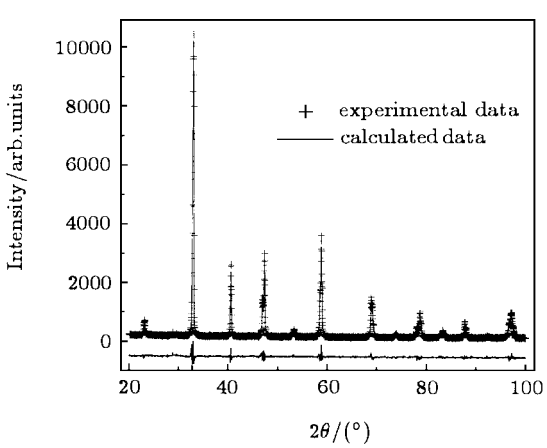


Fig.1. The refinement results for the LSMO sample.

3. Results and discussion

Figure 2 shows the temperature dependence of the magnetization (M–T) measured under a field of $\mu_0 H$=0.02T with increasing temperature from 5 to 400K in the zero-field-cooling and field-cooling modes, respectively. A peak (at about 240K) appears in the M–T curve followed by a weak FM-to-PM transition at T_C (about 375K). The difference between the zero-field-cooling and field-cooling M–T curves can be observed below the magnetization-peak temperature (T_N). The magnetic moment per formula unit as a function of the applied field (M–H) was measured at 5K and 300K, respectively. As shown in the inset of Fig.2, the magnetic moment exhibits a steep jump under a low field, indicating the existence of the FM phase, and then a linear increase with the applied field when $\mu_0 H > 0.5$T. A rough estimate shows that the magnetic moment per formula unit (μ_{exp}=0.23μ_B at 5K, μ_{exp}=0.51μ_B at 300K) is far from the saturation value (μ_{cal}=3.45μ_B) even under a field of $\mu_0 H$=5T. The large difference between μ_{exp} and μ_{cal} suggests that there is a weak magnetic phase in addition to the FM phase. The 5K and 300K M–H curves coincide with each other below, and not above, 0.5T. It can be concluded that the application of a $\mu_0 H$=0.5T field aligns the magnetic moments in the FM region along the magnetic field direction basically, and the increase of the magnetization at 300K up to 5T field can be attributed to the contribution of the weak magnetic phase. At 5K, if the small magnetic moment of the weak magnetic phase is negligible compared to that of the FM phase under a field of $\mu_0 H$=5T, the fraction of the FM phase can be evaluated approximately to be about 7%, based on the μ_{exp}/μ_{cal} ratio.

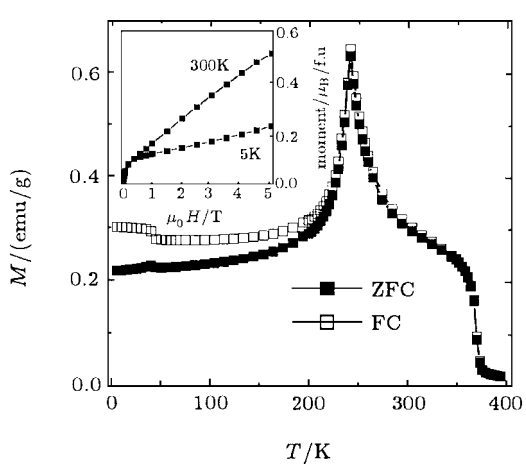


Fig.2. Temperature dependence of the magnetization measured under a field of 0.02T from 5 to 400K during the warming process in zero-field-cooling and field-cooling modes. The inset in Fig.1 shows the magnetic moment per formula unit as a function of the applied field at 5K and 300K.

The ESR spectra were measured from 120 to 400K in a field-sweeping mode (0–8 $\times$ 10^{-1}T). As shown in Fig.3, above T_C, the ESR signals consist of a single peak which has a lineshape close to Lorentzian with a Lande factor g=2.0 nearly independent of temperature. This signal has been believed to be due primarily to PM Mn ions.[26] Below T_C, there is a clear extra FM resonance peak deviating from the resonance field position with g=2.0 and shifting to low fields. With further decreasing temperature below T_N, the original peak with g=2.0 disappears, but the FM resonance peak still exists. As we know, the AFM resonance peak cannot be observed in our measurement condition. Obviously, the ESR and magnetization data (M–T and M–H) suggest that an AFM-to-PM transition occurs near 240K. In other words, the magnetization and ESR measurements prove that PS occurs in LSMO, the FM and AFM phases coexisting below the T_N and the FM and PM phases coexisting when the temperature lies between T_N and T_C.

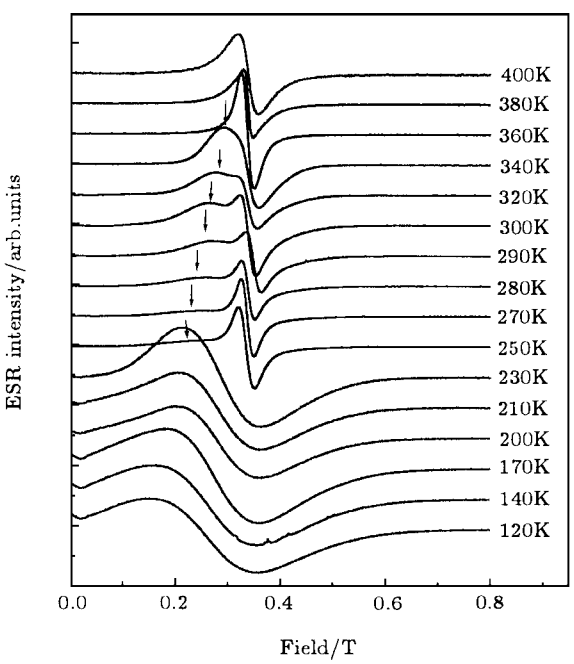


Fig.3. ESR spectra measured from 120 to 400K in the field-sweeping mode from 0 to 8×10^{-1}T.

The coercivity of LSMO was measured and found to be approximately zero when the temperature approached T_N. As a consequence, we cannot obtain the intrinsic magnetic domain structure of LSMO by MFM at room temperature. However, it is possible to obtain the size and shape of the FM phases because the FM phases can cause a strong sign for the MFM, but PM phases cannot. The topography and magnetic force images of the LSMO and $La_{0.67}Sr_{0.33}MnO_3$ (for comparison) were obtained under a zero applied field using MFM with a hard Co-alloy-coated silicon tip magnetized along the tip axis, perpendicular to the polished sample surface. The lift height was 30nm during the measurement for magnetic force images. As shown in Fig.4(b), for $La_{0.67}Sr_{0.33}MnO_3$ which is FM at room temperature, the bright and dark regions, representing magnetic domains with anti-parallel magnetization perpendicular to the measured surface, are distributed homogeneously in the MFM image. The MFM image of LSMO (Fig.4(d)) is very interesting. We observed some black circular regions with mesoscopic sizes embedded in the background that cannot cause the MFM sign. Contrasting the topography and magnetic force images, it is obvious that the magnetic inhomogeneity observed in the right image is not due to topography. We believe that the local black regions are FM and the remaining parts are PM at room temperature. The magnetic tip magnetized the FM regions due to the proximate zero coercivity of the FM phase at room temperature, which results in an attractive force between the tip and the FM regions. As a result, we cannot observe white regions, but only the black regions. In a sense, the brightness of the local black regions can reflect the depth of the FM phase embedded in the LSMO sample. The proportion between the FM and the PM phases evaluated from the MFM image is in accordance with the magnetization measurements based on the ratio μ_{exp}/μ_{cal}. According to the MFM image of the LSMO, the maximum size of the FM phase is about 0.7μm, which is too large to be explained by the charge segregation type PS. Therefore, we prefer to consider that the PS in the LSMO is electroneutral. As is well known, $Ln_{1-x}A_xMnO_3$ is apt to be oxygen-rich for $x \leq 0.2$ and oxygen-poor for $x \geq 0.5$. In low-doped regions, for example in $La_{1-x}Ca_xMnO_3$ with $x \leq 0.2$, the excess oxygen is distributed inhomogeneously in the whole sample. The regions enriched with oxygen have an enhanced hole density and the holes establish local FM ordering.[25,26] The PS is of the electroneutral type because the densities of holes and excess oxygen are the same in the given region. For high-doped regions, such as LSMO, we propose that oxygen vacancies have a tendency to concentrate and decrease the local Mn^{4+} content to create the FM ordering around them. As a consequence, electroneutral PS occurs in LSMO.

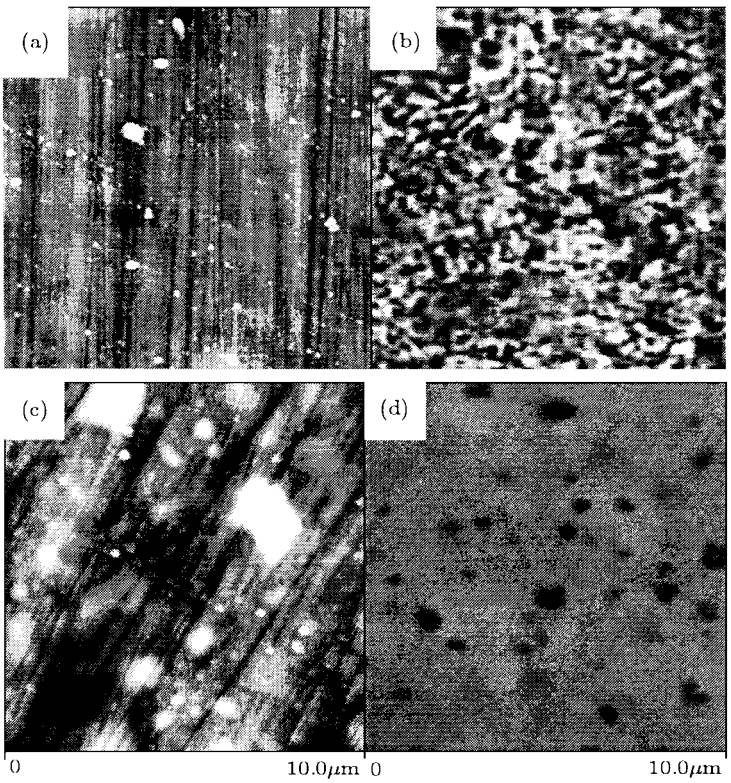


Fig.4. Topography and magnetic force images for $La_{1-x}Sr_xMnO_3$ with x=0.33 (a), (b) and 0.55 (c), (d) at room temperature.

4. Summary

In summary, through ESR, MFM and magnetic measurements, PS has been found in the highly Sr-doped $La_{1-x}Sr_xMnO_{3-\delta}$ (x=0.55). FM and AFM phases coexist at low temperatures; FM and PM phases coexist when the temperature is between T_N and T_C. The results of the MFM suggest that PS in LSMO is not of charge segregation type, but of an electroneutral type due perhaps to the nonuniform distribution of oxygen vacancies.

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