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ESR and Magnetization Study of $La_{0.7}Ca_{0.3}MnO_3$

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Electron spin resonance and magnetization measurements were carried out on $La_{0.7}Ca_{0.3}MnO_3$ in the ferromagnetic as well as paramagnetic phases. Evidence of an inhomogeneous magnetic structure, consisting of ferromagnetic microregions embedded in an antiferromagnetic matrix near T_c, as well as similar local magnetic structures above and below T_c, were found.

1. Introduction

Perovskite manganites with mixed manganese valence, $La_{1-x}D_xMnO_3$, with D being a divalent metal, have attracted a great deal of attention due to the anomalously large negative "colossal" magnetoresistance (CMR) for $0.2<x<0.5$ 1-5]. In this composition range, the system shows the simultaneous appearance of metallic conduction and ferromagnetism at low temperatures, while the end materials (x=0, 1) are insulating antiferromagnets. The underlying physics of this system has been traditionally explained in terms of the double exchange (DE) mechanism due to Zener [6-8]; however, recent works have shown that the DE alone may not be sufficient to explain the phenomenon. Other effects such as lattice polarons due to the Jahn-Teller (JT) distortion [9], magnetic polarons, and electron localization [10] have been advanced. One interesting proposal is that the phase separation of carriers, already seen in other systems [11], is an essential ingredient in understanding CMR materials [12].

Several computational works have indicated that a homogeneous state is unstable against phase separation (PS) as charge carriers are doped into manganites [13-15]. It was also shown that the inclusion of Coulomb interactions leads to a charge-inhomogeneous state with clusters of one phase (high carrier density) embedded in the other (low carrier density). Since inhomogeneity in the carrier density also gives rise to corresponding inhomogeneity in the magnetic structures, the PS state consists of ferromagnetic metallic clusters surrounded by either antiferromagnetic regions or by paramagnetic insulators [12]. Thus, a detailed microscopic study of the magnetic properties of perovskite manganites should shed light on the PS model.

Currently, evidence for the inhomogenous nature of perovskite manganites is offered by several studies, including NMR [16-18]. However, electron spin resonance (ESR), which directly probes the electron spins, is the most suitable means for this purpose. A few ESR studies have already been carried out, and spin clusters and the inhomogeneous nature of the doped manganites have been suggested by some ESR works [19-21]. Up to now, most of the ESR studies have been carried out on powder or thin film samples, as a sample dimension greater than the skin depth at the microwave frequency gives rise to asymmetric ESR lineshapes [22, 23]. While the absolute values of the g_{eff}-value and the linewidth may be less reliable, the asymmetric lineshape can give more information on the inhomogeneity of the sample [23]. Rettory *et al.* have performed an ESR experiment on a $La_{0.7}Ca_{0.3}MnO_3$ single crystal sample whose size was larger than the skin depth at the microwave frequency, and obtained asymmetric lineshapes. However, they did not fully discuss the asymmetry of the lineshape. Furthermore, to our knowledge there is no report of a comprehensive ESR study of bulk samples of CMR materials covering a wide temperature range both above and below the ferromagnetic transition temperature (T_c).

In order to carefully examine the local magnetic properties related to the inhomogeneous nature of CMR systems, we have made systematic ESR measurements and quantitative analysis for a bulk sample of a representative CMR material, $La_{0.7}Ca_{0.3}MnO_3$ (LCMO), covering a wide temperature range both above and below T_c. A careful dc magnetization measurement was also carried out just above T_c in order to find a relation between the macroscopic and microscopic inhomogeneous magnetic properties. As a result of the comprehensive study of this unique system, we observed for the first time that the microscopic magnetic structures are very similar above and below T_c, except for the long range ordering. Furthermore, an antiferromagnetic correlation as well as ferromagnetic clusters were explicitly revealed in this work.

2. Experiment

The $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) sample used in this work was prepared by the standard solid state reaction method from 99.9% purity oxide and carbonate powders. X-ray diffraction analysis showed a single phase perovskite structure of pseudo-cubic symmetry with a lattice constant a=3.867 Å[25]. The resistivity was measured using a standard four-probe method. In order to examine the physical properties associated with the spin ordering transition, the dc magnetization was measured with a superconducting quantum interference device (SQUID) magnetometer as a function of temperature, and as a function of magnetic field at 250 K, which is in the paramagnetic regime. The magnetic ordering temperature is conventionally defined to be the onset of the ferromagnetic magnetization, which gave a T_c of 235 K for our sample, in good agreement with the conductivity measurements. The sample dimension was greater than the calculated skin depth at room temperature, and the ESR measurements were made at 9.4 GHz employing a Bruker ESP 300E spectrometer using a microwave power of 1 mW and a modulation amplitude of 5 G.

3. Results and Discussion

Typical differential ESR spectra for our sample are shown in Fig. 1. As can be seen, the ESR spectra are of an asymmetric lineshape both above and below T_c. Three main parameters were defined as depicted in Fig. 1; the asymmetry parameter (AP), the g_{eff}-value, and the linewidth. The AP, defined as the ratio of the positive to the negative maximum (A/B) in the differential ESR lineshape, serves as a clue to determine the homogeneity in the sample [22, 23].

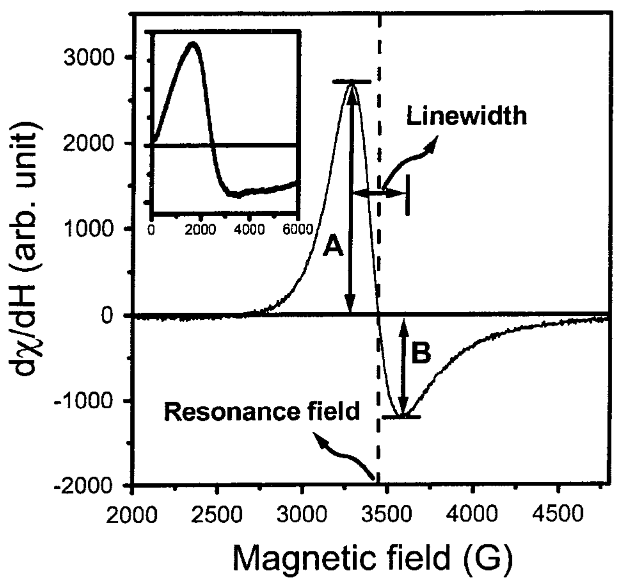

Fig. 1. Typical differential ESR spectrum above T_c (300 K) showing how the parameters were defined. The inset depicts a typical differential ESR spectrum below T_c (163 K).

The resonance field is determined from the zero crossing point of the ESR spectrum, and the g_{eff}-value is obtained from the equation.

$$g_{eff} = \frac{h\nu}{\mu_B H_{res}} \quad (1)$$

where ν is the microwave frequency, μ_B is the Bohr magneton, and H_{res} is the resonance field. However, the ESR parameters could not be determined unambiguously in the temperature range between 185 K and T_c, which is attributed to the combined effect of the Q-factor change in the cavity due to the large magnetoresistance during the ESR measurements [26], and the coexistence of signals characteristic of the high temperature and low temperature regimes well above and well below T_c, respectively.

The minimum AP value for a homogeneous sample is 2.7, which corresponds to the slow diffusion limit, except when the sample dimension is smaller than the skin depth, which is not the case here. On the other hand, Fig. 2 shows that the AP value is about 2.0 above T_c, without a temperature dependence. For an inhomogeneous sample, localized spins confined to the surface of the sample will give rise to AP=1, whereas AP is expected to be 2 for localized spins randomly distributed throughout the volume [23]. Using a combination of volume thermal expansion, magnetic susceptibility, and small-angle neutron scattering, De Teresa *et al.* indicated the existence of ferromagnetic microregions in the paramagnetic regime [13]. When the ferromagnetic moments coexist with the paramagnetic moments, the ferromagnetic moments make the major contribution to the ESR intensity. Thus, the temperature-independent AP value of

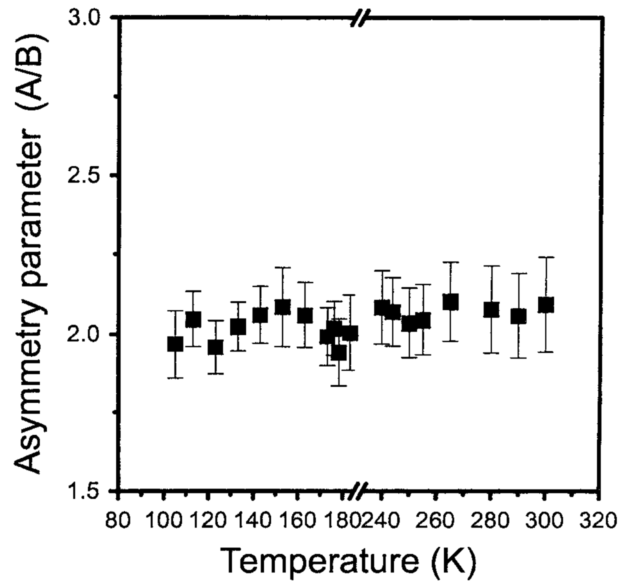

Fig. 2. Temperature dependence of the ESR lineshape asymmetry parameter. Essentially the same asymmetry parameter both above and below T_c strongly suggests that the microscopic local magnetic structures above and below T_c are qualitatively similar except that the latter carries long range order.

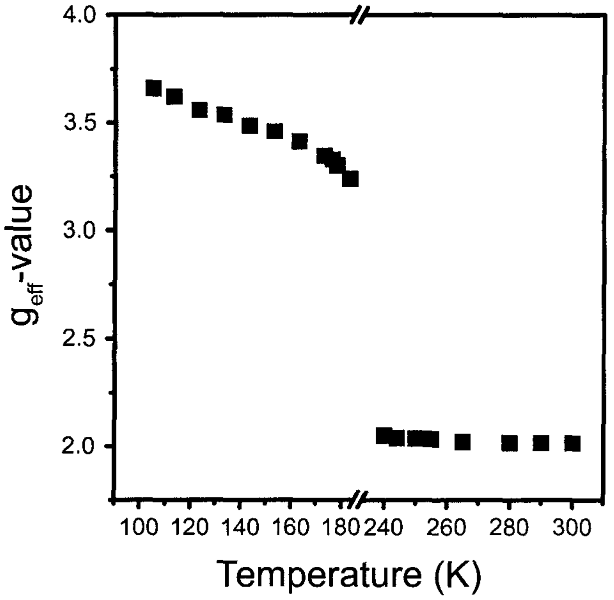

Fig. 3. Temperature dependence of the effective g-value. The error bars are within the size of the data points. Above T_c the g_{eff}-value is very near the free electron value of about 2, indicative of relatively weak interaction between the ferromagnetic microregions. On the other hand, the marked increase with decreasing temperature below T_c is attributed to the rapidly growing interaction between the ferromagnetic microregions and their alignment with one another.

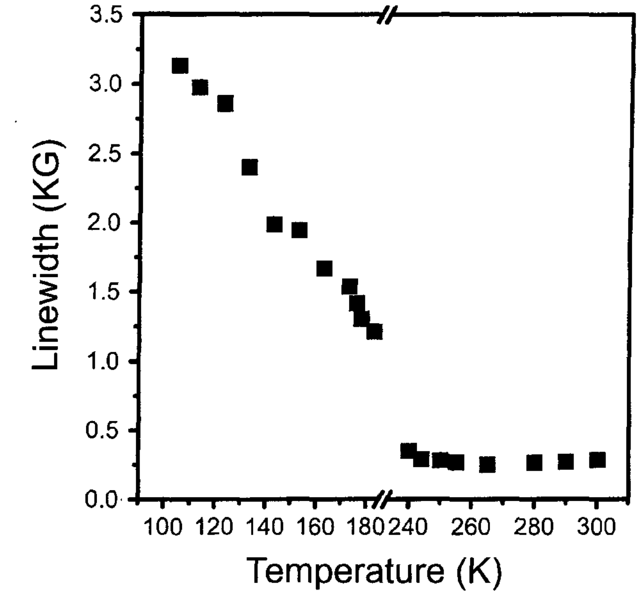

Fig. 4. Temperature dependence of the peak-to-peak ESR linewidth. The error bars are within the size of the data points. The prominent increase in the linewidth with decreasing temperature below T_c corresponds to a more inhomogeneous local magnetic field distribution, with the ferromagnetic microregions growing more inhomogeneous as the temperature is lowered.

about 2 indicates that the ferromagnetic microregions, acting as the ESR centers, are randomly distributed throughout the volume of the LCMO. According to the PS model, the LCMO is separated into two regions; one of them the hole-rich metallic region, the other the hole-poor insulating region. The hole-rich metallic regions are expected to have ferromagnetic properties and to play the role of magnetic impurities above T_c. It is noticed that the AP values obtained in this work are in good agreement with the existence of magnetic clusters, which follows from the PS model. The PS model also suggests that the phase separation persists below T_c, presumably with the hole-poor regions remaining paramagnetic or antiferromagnetic, which is supported by the fact that the AP values are below T_c are the same as those above T_c. Indeed, as shown in Fig. 2, it is remarkable to note the AP values below 185 K, which are also about 2 within the error limits. Thus, AP values essentially the same both above and below T_c are in excellent agreement with the PS model.

Fig. 3 shows the temperature dependence of the effective g-value (g_{eff}), corresponding to the magnetic field of the maximum microwave absorption. While the absolute values may not be quite reliable, the relative values are reliable because of the temperature independent AP. The g_{eff}-values above T_c are very near the free electron value of about 2, which is indicative of relatively weak interactions between the ferromagnetic microregions. On the other hand, the value of g_{eff} exhibits a marked increase with decreasing temperature below T_c, corresponding to rapidly growing interactions between the ferromagnetic microregions leading to their alignment in one direction.

As the temperature is lowered below T_c, the ferromagnetic microregions can be expected to grow into the nearby hole-poor regions, random in their shape and distribution, and to align with one another. In this scenario, the local magnetic fields would become more inhomogeneous with decreasing temperature, the ESR linewidth thus becoming broader. A prominent increase of the peak-to-peak linewidth with decreasing temperature below T_c, which can be seen in Fig. 4, supports this scenario. Furthermore, using neutron scattering experiment, Lynn *et al.* indicated that the ferromagnetic transition in LCMO is not driven by the thermal excitation of spin waves as for a conventional ferromagnetic transition, but rather is driven by the spin diffusion mechanism [16]. This unconventional ferromagnetic transition also is compatible with our scenario. Thus, we suggest that the isolated ferromagnetic microregions start to grow and start to interact with each other near T_c. Upon increasing sizes of the metallic regions and their alignment with an applied external magnetic field, the conductivity will dramatically increase as well as the magnetization, resulting in the colossal magnetoresistance.

In order to elucidate the nature of the magnetic structures, we have made a careful measurement of the field dependent magnetization at a temperature, 250 K, *above* T_c (235 K). While a linear dependence is seen for low magnetic fields in Fig. 5, a nonlinearity is evident for high fields. In particu-

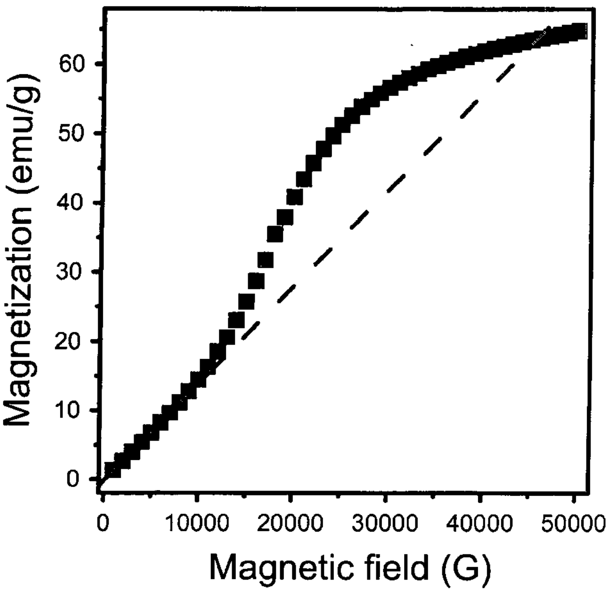

Fig. 5. Magnetic field dependence of the magnetization at 250 K, above T_c (235 K). The error bars are within the size of the data points. The inflection at around 1 T indicates an antiferromagnetic correlation. This magnetic field dependent magnetization suggests that the structure of the phase separated state consists of ferromagnetic microregions surrounded by insulating antiferromagnetic regions.

lar, it is quite interesting to note an upward inflection at a critical field of about 1 T, which can only be explained by supposing an antiferromagnetic correlation in the system. In other words, this upward inflection can naturally be attributed to spin-flips in the antiferromagnetic insulating regions, which are induced by magnetic fields greater than a critical strength. For high enough magnetic fields, the magnetization shows a saturation behavior as would be expected. Given the ferromagnetic regions in the LCMO, it is quite reasonable to interpret the structure of the PS state as consisting of ferromagnetic microregions surrounded by insulating antiferromagnetic regions.

In summary, we have studied the nature of spin systems in a $La_{0.7}Ca_{0.3}MnO_3$ bulk sample showing colossal magnetoresistance by means of electron spin resonance and magnetization measurements. Our data provided convincing experimental microscopic evidence for the the phase separation model, and revealed a detailed magnetic structure of ferromagnetic microregions surrounded by antiferromagnetic insulating regions both above and below T_c.

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