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A microwave absorption study in the thermochromic $SrMnO_3$

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Abstract

We report electron paramagnetic resonance (EPR) and magnetically modulated microwave absorption spectroscopy (MAMMAS) studies at X-band (8.8–9.6 GHz) on powdered $SrMnO_3$ in the 90–400 K temperature range. EPR spectrum shows one broad single-line at room temperature, which is observed only above 280.5 K, being compatible with an antiferromagnetic order. The onset of the para–antiferromagnetic transition has been determined from the temperature dependence of three main parameters extracted from the EPR spectra: resonant field (H_{res}), peak-to-peak linewidth (ΔH_{pp}) and integrated intensity (I_{EPR}). The MAMMAS response shows a change in the region 276–283 K, compatible with the para–antiferromagnetic transition, without presenting any significant change in the region of thermochromism.

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Keywords: Electron paramagnetic resonance (EPR); Manganite; Magnetic transition

1. Introduction

Some ceramic materials with perovskite-type structure and general formula ABO_3 have been extensively studied because of their interesting electric and magnetic properties [1]. Particularly, there is a renewed interest in manganese-based perovskites due to the colossal magnetoresistance (CMR) [2] exhibited near the magnetic ordering of Mn spins. CMR refers to the large negative change in the resistivity of the material on the application of a dc magnetic field. The magnetic and electronic properties have been traditionally examined within the framework of double exchange, which considers the magnetic coupling between Mn^{+3} and Mn^{+4} ions. Manganites of several rare earth and other transition metals are being studied because of their ferroelectric and, in some cases, multiferroic nature [3], which may lead to a whole range of new applications [4].

Recently, thermochromism has been observed [5] in manganese-based oxides materials: $BaMnO_3$ and $SrMnO_3$ (SM). These materials present a change of color at low temperatures (about 140 K). It was established by X-ray diffraction (XRD) and transmission electron microscopy that the thermochromism is not due to a structural phase change; therefore there must be another mechanism giving rise to thermochromism in these materials. Additionally, the manganites of Na, K, Mg, and Ca are not thermochromic.

The electron paramagnetic resonance (EPR) spectra provide important information concerning the homogeneity of the sample [6], the spin-dynamics [7], and Jahn–Teller polaron formation [8] in manganites. EPR spectra on CMR materials show some characteristic features, e.g. the peak-to-peak linewidth (ΔH_{pp}) are large and show a minimum close to the ferromagnetic transition temperature. In addition, Shengelaya et al. [9] noticed in these materials a close similarity in the temperature dependence between ΔH_{pp} and the conductivity. Some investigations have dealt with charge-ordered transition in manganites

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[10,11], i.e., a real-space ordering, as a function of temperature, of Mn^{+3} and Mn^{+4} ions.

The magnetically modulated microwave absorption spectroscopy (MAMMAS) has been used successfully for the detection of superconducting transitions [12,13]. Recently, this technique also has been used to detect the ferromagnetic transition in magnetic [13–15] and magnetoresistive materials [16,17]. The MAMMAS technique is based on temperature variations of the modulated microwave absorption, and provides a high-sensitive detection of magnetic order; this temperature profile of the modulated microwave absorption can also provide valuable information about the nature of magnetic ordering. Also, the MAMMAS technique can distinguish between different dissipative dynamics of microwave absorbing centers [13–15,17].

In this work, we focus on the study of the changes in the EPR spectra of SM manganite; in particular, the resonant field (H_{res}), ΔH_{pp} and integrated intensity (I_{EPR}) as a function of temperature from 400 to 90 K are closely examined. An investigation of the magnetic transition in this material by the MAMMAS technique is presented.

2. Experimental procedure

SM powders were prepared by the standard solid-state reaction method. XRD analysis was carried out with a Philips X'Pert diffractometer using the 1.5406 A CuK_α line to check phase purity. Samples of this material showed to be in single phase [5]. Since thermochromism occurs at very low temperature (~140 K), it may be observed directly by immersing the sample in liquid nitrogen (77 K) as a quick test.

The EPR measurements were performed using a JEOL JES-RES 3X spectrometer operating at X-band with 100 KHz modulations, with field sweep from 0 to 8000 G. Sample was placed in the center of a TE_{011} cylindrical cavity (at maximum magnetic field and minimum electric field). The temperature range was from 400 to 90 K and EPR spectra were recorded while cooling the sample. The spectrometer was modified by connecting the X and Y inputs to a PC, enabling digital data acquisition [13].

The microwave absorption investigation uses the same EPR spectrometer, adequately modified [13]. The microwave response with modulation of a magnetic field is measured. The MAMMAS response was recorded while the temperature of the sample is scanned, with very slow temperature sweeps (~1 K/min), while a constant magnetic field of 600 G (H_{dc}) was applied with an amplitude of modulation field (H_{mod}) of 4 G and an incident microwave power of 7 mW.

3. Results and discussion

Fig. 1 shows that the MAMMAS signal increases monotonically as temperature decreases from 400 to 283 K. In this temperature range the material is paramagnetic [18] and the paramagnetic microwave absorption increases with the decrease in temperature [14,17]. Our MAMMAS measurement is in agreement with the interpretation that this absorbing process is due to paramagnetic dipoles.

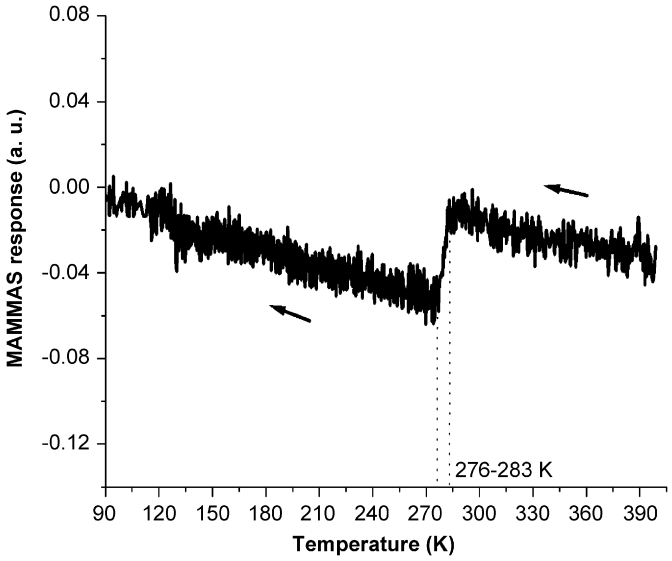

Fig. 1. MAMMAS spectrum for $SrMnO_3$ with applied magnetic field 600 G and modulation 4 G.

MAMMAS response reaches a maximum at 283 K; after that, the microwave absorption decreases very fast with decreasing temperature until $T_N = 276$ K is reached. In addition, at temperatures below ~278 K this system shows an antiferromagnetic (AF) ordering [18], as a result of the linear Mn–O–Mn superexchange interaction between Mn ions in the corner-sharing MnO_6 octahedra of its hexagonal structure. Then, in the 283–276 K region, the microwave absorption decrease is due to the decrease of the quantity of absorbing centers due to the process of antiparallel spin alignment. Below T_N, the MAMMAS spectrum remains approximately lineal with a significant slope; a ferromagnetic impurity in the form of a second phase, with a Curie point close to 276 K and a significant concentration, could explain this non-resonant absorption line. However, a more sound explanation of this behavior can be attributed to the canting of Mn sublattices in the AF matrix in this region of temperature [14]. Two orthogonal oxygen p orbitals bonding to two Mn atoms will, according to Goodenough–Kanamori–Anderson rules [19], result in a weak ferromagnetic cation–anion–cation interaction.

The whole MAMMAS profile follows the variations on the number of absorption centers, which in turn is controlled by the establishment of the AF order and by the presence of a weak ferromagnetism at low temperature. Additionally, the MAMMAS spectrum indicated no phase transition in the region of color change, which is below 140 K.

We now turn to EPR results; Fig. 2(a) shows EPR spectra recorded in the 90–400 K temperature range for SM powders. We observed a single broad symmetric

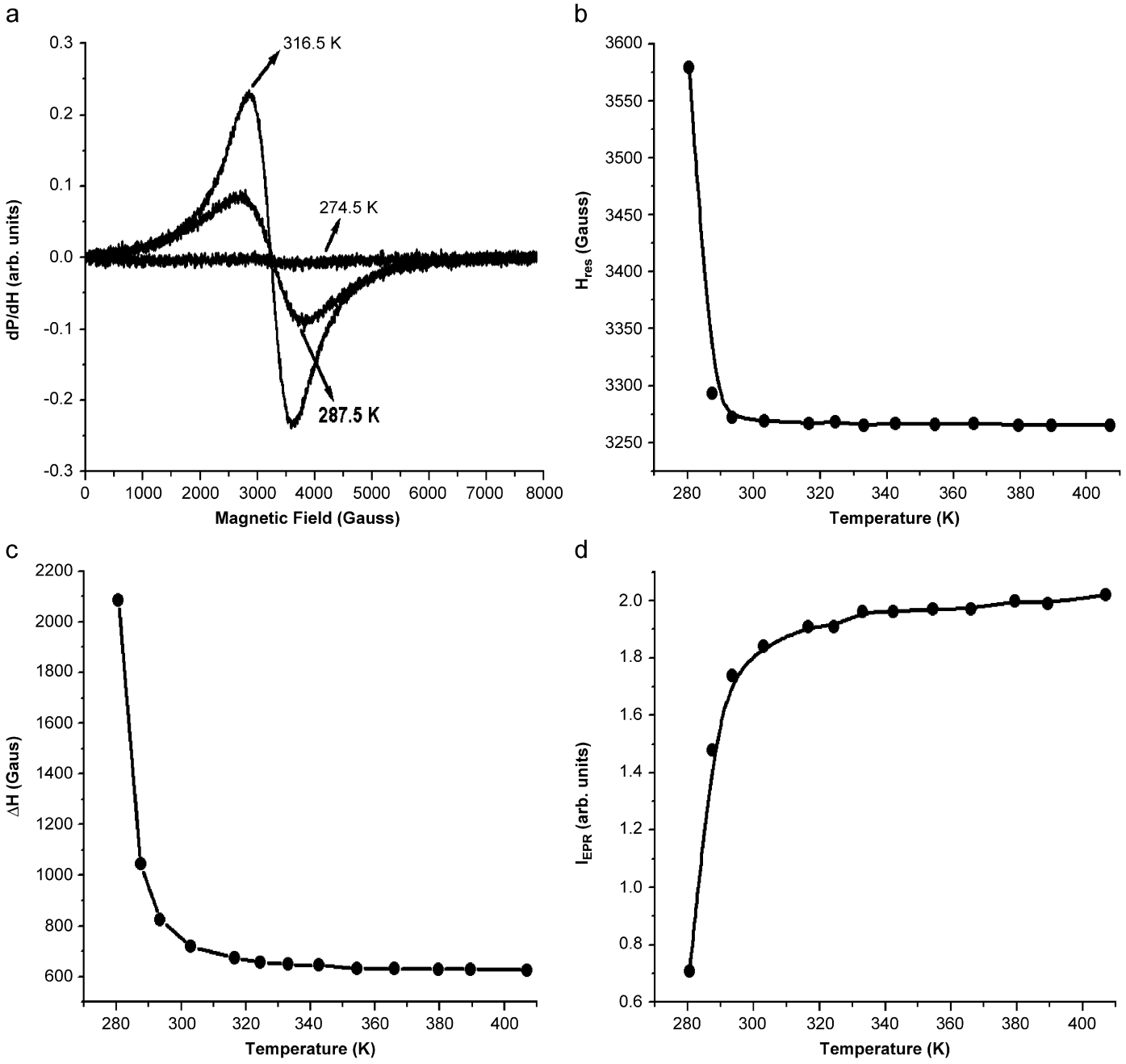

Fig. 2. (a) EPR spectra of $SrMnO_3$ powders for a few selected temperatures. Temperature variation of lineshape parameters: (b) resonant field—H_{res}, (c) peak-to-peak linewidth—ΔH_{pp}, and (d) integrated intensity—I_{EPR}. Curves connecting points are only guides for the eyes.

Lorentzian line, due to exchange-coupled Mn spins. Below ~280.5 K there is no resonant absorption line. The derivative of microwave power absorption with respect to the static field (dP/dH) is fitted into the two-component Lorentzian equation accounting for the contributions from the clockwise and anticlockwise rotating components of the microwave magnetic field [20,21]. The temperature dependences of the EPR parameters obtained from these fits are plotted in Fig. 2(b–d).

As a function of temperature, both H_{res} and ΔH_{pp} show a similar behavior, as seen in Fig. 2(b, c); in other words, H_{res} and ΔH_{pp} increase slightly as temperature goes down from 407 to 303 K. This gradual increase is found to be common to various AF materials [22]. As temperature continues to decrease, H_{res} and ΔH_{pp} have a sudden rise reaching maxima at 280.5 K. This rapid increase might be due to the build-up of magnetic correlations preceding the transition to the long-range AF ordering at T_N, and so, when T approaches T_N, H_{res} and ΔH_{pp} gradually increase; close to T_N, they diverge.

Fig. 2(d) shows that the I_{EPR} decreases slowly with the decrease in temperature until 303 K; then, a rapid decrease occurs. For temperatures lower than 280.5 K no EPR signal is observed because normally an AF resonance is

present only at very high frequencies [23], around 100 GHz or more, far beyond 9 GHz, which is the frequency used in this experiment.

4. Conclusions

MAMMAS measurement for $SrMnO_3$ showed a drastic change of the modulated microwave absorption vs. temperature, which suggested a para–antiferromagnetic transition at $T_N = 276$ K, with a weak ferromagnetism at low temperature. When the EPR spectra of the sample are taken at different temperatures, we see changes in the spectra that confirm the para–antiferromagnetic transition. Around 140 K, EPR and MAMMAS measurements have not been able to detect any change in the magnetic moments or in the crystalline field. Then, the mechanism for thermochromism remains unsolved and seems unrelated to magnetic order transition and/or crystal field transitions.

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