

## Heating of manganites by magnetic component of microwave

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When the dependence of EPR spectra of  $\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$ ,  $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ ,  $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$  and  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  on microwave power (1-200mW) applied in the EPR instrument was investigated, it was observed that the samples became unusually hot on high microwave power levels. The cause of heat generation has been explained as interaction of the spin of  $e_g$  electron of  $\text{Mn}^{3+}$  with the magnetic component of microwave field which ultimately leads to Debye type of relaxation of a physical ensemble, i.e., spin-orbital-lattice polaron. The polaron so created is found to be of 11 Å size and consists of  $\text{Mn}^{3+}$  ion, its nearest neighbours  $\text{Mn}^{4+}$  and  $\text{La}^{3+}$  ions and the alkaline earth ions along with oxygen octahedra surrounding Mn-ion sites.

**Keywords:** Manganites, Electron paramagnetic resonance, Microwave heating

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### 1 Introduction

$\text{Re}_{1-x}\text{B}_x\text{MnO}_3$  (where Re=La, rare earths and B=Pb, Ba, Sr, Ca etc.) manganites have recently become important because of their potential applications in technology and as a challenge to understand their true nature. They have correlated lattice, charge and spin degrees of freedom and a complex phase diagram<sup>1-4</sup>. Probably they are affected by the interplay of all degrees of freedom in solid state physics. The structure, magnetic and electronic properties are influenced by Goldschmidt tolerance factor and the Jahn-teller distortion<sup>5-10</sup>. Zener<sup>11</sup> was the first to give explanation of FMM state of manganites by double exchange (DE). Later Millis *et al*<sup>12,13</sup> found that DE alone is not sufficient to explain its behaviour and invoked electron-lattice coupling to explain the experimental data. Strong interactions between spin and orbital polarons have been observed and composite object like orbital-spin-lattice polaron has been detected<sup>14</sup>. The most important property of manganites is the colossal magnetoresistance (CMR).

Recently, the dependence of electron paramagnetic resonance (EPR) spectra of some manganites near optimal doping ( $\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$ ,  $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ ,  $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$  and  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  shown as  $\text{Pb}_{0.67}$ ,  $\text{Pb}_{0.4}$ ,  $\text{Ba}_{0.3}$  and  $\text{Sr}_{0.33}$  respectively) on microwave power used in the instrument for the observation of spectra has been investigated. The EPR spectra showed strong dependence on microwave power level. While doing the experiments, it was

observed that after recording spectra at higher microwave power levels, the samples became unusually hot. It was verified that the changes observed in the spectra on increase of power were actually due to heating effect of microwave power. Heating of materials by microwave power is a very usual phenomenon in which the electric component of the microwave electromagnetic wave interacts with the electric dipole moments of the molecules or their parts. This interaction is the strongest when the natural frequency of the rotation of molecules (Debye relaxation) is nearly equal to the frequency of the irradiating wave. The electrical component of microwave forces the molecules to follow it which experience frictional forces and thus heat is generated.

But in the present case, the situation is quite different. In our EPR set-up (RE-2X, JEOL, JAPAN), the cylindrical microwave resonant cavity is in  $\text{TE}_{011}$  mode and only the magnetic component of microwave is incident on the sample, the electrical component being non-existent in the space occupied by the sample. Then the question is what causes the sample to be heated? We mainly address this problem in this paper along with some other measurements such as resistivity versus temperature and magnetic susceptibility versus temperature.

### 2 Experimental Details

Samples investigated in the present work are some of those whose partial study has been reported

in Ref. (15). In the present paper, following experimental works have been carried out: (1) Magnetic susceptibility versus temperature of the substances equivalence of the effect of direct heating and microwave heating of samples on the EPR spectra and (3) measurement of resistivity versus temperature of the substances. The pellets of the substances fitted with the arrangements of four-probe resistivity measurement method were dipped in liquid nitrogen and taken out. The temperatures and resistances of the pellets were measured simultaneously. The whole process took 4-5 minutes as the room temperature was attained in that time span and thus enough time was not allowed between the successive measurements for sufficient number of electrons to jump from the valence band and settle in the conduction band specially near the impurity exhaustion region. In the present work, measurement of resistivity versus temperature and also susceptibility versus temperature of each sample took more than six hours to ensure the equilibrium states of the substances.

The experimental method by which equivalence between direct heating and microwave heating was established is described below. Once the EPR spectra of a sample were monitored at different microwave levels and next time, the spectra of the same sample were monitored at different temperatures by direct heating keeping the microwave power level at 1-2 mW. It was observed that similar changes took place in the two cases. The next problem was to find out numerical relationship between the applied microwave power level and increase in the temperature of the sample. It was not possible to introduce a thermocouple to measure the temperature along with the sample because in that case the 'Mode' in the apparatus was totally disturbed and the apparatus could not operate. To get over this difficulty, the electrical resistance of the samples kept in the cavity was measured by changing microwave power levels in steps keeping the apparatus in the 'Mode' regime and next the resistance of the samples (kept in the same settings but the microwave power level at the minimum, (1-2 mW) were measured on raising the temperature by direct heating. By comparing resistances of the samples measured in these two ways, a relationship between microwave power level and temperature could be established. A nearly linear relation was found which is as follows: the temperature of the sample = initial temperature of the sample +  $2/5$  (microwave power expressed in mW).

It means that on application of the full microwave power (200 mW available in the instrument), the temperature of the sample could be increased by  $[80^{\circ}\text{C}]$ . In our experiments, the temperature of the samples varied from 295K (initial) to 375K (final). Equivalence between microwave heating and direct heating will be shown by measuring the resistances of two samples  $\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$  and  $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ .

Unless special precautions are taken, experimentally it is quite difficult to measure electrical resistance of a sample by four-probe method with the microwave power on, because all the paraphernalia needed for four-probe method along with the sample inserted into the cavity would greatly disturb the 'Mode'. In the present case, a very thin refill of a ball-point pen was used as a sample holder, on which a thin (0.5 mm. in width) piece of a pellet of the sample (2-3 mm. in length) was pasted and four very thin wires (single strands of flexible wire) were connected at four equidistant points on the pellet through silver paste; the other ends of the four wires were taken out of the cavity and connected to current source and voltmeter. To give strength or to avoid disconnection of the wires from the sample during pulling out or insertion of the sample holder in the cavity, the wires were pierced through the sample holder at appropriate places before connecting them to the sample. Even with these precautions, the 'Mode' was a little broadened and reduced in size but  $80^{\circ}\text{C}$  rise in temperature could be achieved.

In the case of direct heating of the sample, heated nitrogen gas was passed in a controlled way through the cavity. The temperature of the sample was taken as the mean of the gas temperature at the inlet and the outlet of the cavity. For measuring the rise of temperature either by microwave power or direct heating, 2-3 min of waiting time was given.

It was verified that the temperature increase by microwave power was the same whether the instrument was kept in the 'Mode' regime or 'Operation' regime. Most of the measurements were done by keeping the instrument in the Mode regime. It was further verified that the EPR spectra of any sample did not change with or without the fittings required for the resistance measurement by the four-probe method.

### 3 Results and Discussion

The results of resistivity versus temperature measurements are shown in Fig. 1. Because of the different conditions in which the  $R$ - $T$  curves were

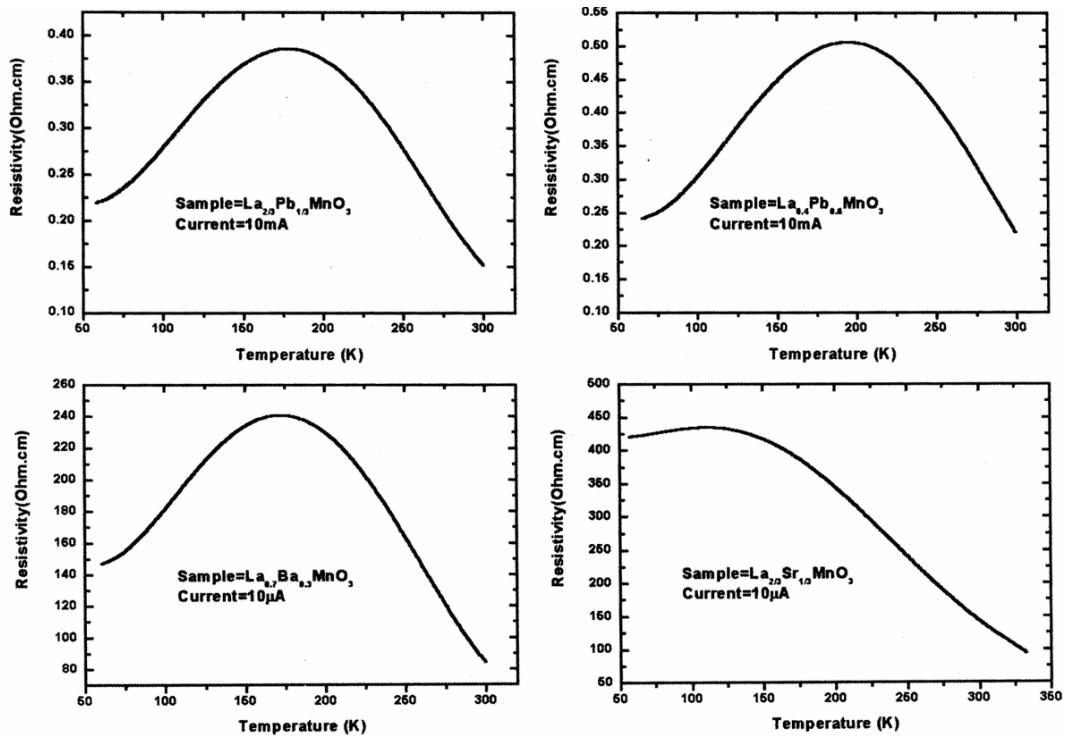


Fig. 1—Resistivity versus temperature graphs

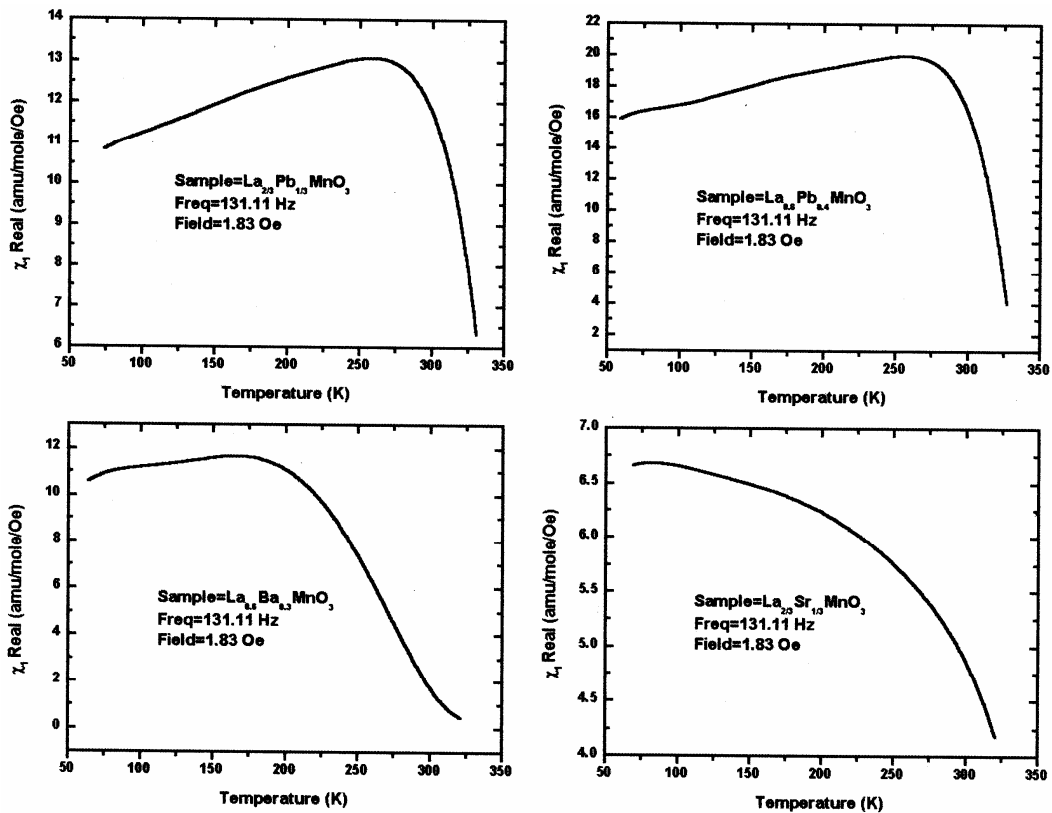


Fig. 2—Real part of magnetic susceptibility versus temperature graphs

recorded in the present case and those reported in Ref. (15), there is one significant difference between the two. In the curves of the Ref. (15), there appears a kink at the point C, whereas the curves in the present case are smooth. The region near C corresponds to the impurity exhaustion region in the extrinsic semiconductors in terms of which the curve after  $T_c$  has been interpreted. In the curves of Ref. (15) the successive readings have been taken at intervals of 10-15 sec and in the present case at intervals of 2-3 min. Near the impurity exhaustion region, a few charge carriers will be able to reach the conduction band from the valence band in short time interval of 10-15 sec, but if more time is allowed (2-3 min) sufficient number of charge carriers can be populated in the conduction band and thus affecting conductivity. Hence, the curves in Ref. (15) appear with kinks but those in the present case are smooth. This was the justification for showing the new  $R-T$  curves here. The results of real part of magnetic susceptibility versus temperature measurement are shown in Fig. 2.

The transition temperatures ( $T_c$ 's) measured from the mid-point of the fall of the respective quantities in the two figures are of the same order. For example, the transition temperatures ( $T_c$ 's) from the  $\rho-T$  curves are  $Pb_{0.33}$  (~250K),  $Pb_{0.4}$  (~270K),  $Ba_{0.3}$  (~260K), and  $Sr_{0.33}$  (~240K).  $T_c$ 's from the susceptibility curves are  $Pb_{0.33}$  (~290K),  $Pb_{0.4}$  (~290K),  $Ba_{0.3}$  (~260K) and  $Sr_{0.33}$  (~275K). Small differences in  $T_c$ 's in the two cases may be due to different roles of ferromagnetic clusters which survive beyond  $T_c$ 's,

Equivalence between microwave heating and direct heating as indicated by the electrical resistances of  $Pb_{0.33}$  and  $Pb_{0.4}$  are shown in the Fig. 3.

The important question to be answered is how microwave field can heat a substance when only its magnetic component is incident on the substance. There is one possibility that the magnetic component perturbs the spin of the  $e_g$  electron of the  $Mn^{3+}$  ion and the effect is transferred to its orbital angular momentum by l-s coupling and further transferred to orbital angular momenta of the electrons of the nearest ions. If l is disturbed, it may disturb the orientation of the molecules. Thus, molecular orientation or their dynamics can be disturbed indirectly by the disturbance of spin. Thus, by affecting the motion of spin by magnetic component of microwave field, a physical body can be put into motion, which may generate heat. But again this effect is observable only when the natural frequency of motion of this body is equal to the frequency of the impressed field. Microwave frequency in X-band EPR instruments (as in the present case) is  $\sim 10^{10}$  cycles/sec. or time period  $\sim 10^{-10}$  sec. Silvana Mercona *et al*<sup>16</sup>. have measured the dielectric relaxation time of  $Pr_{0.67}Ca_{0.33}MnO_3$  and found that it is  $\sim 10^{-10}$  sec. at  $\sim 300$ K. Further, Schelschmidt *et al*<sup>17</sup>. have found the real part of the dielectric constant of  $Pr_{0.65}Ca_{0.28}Sr_{0.07}MnO_3$  to be more than 60 at  $\sim 300$ K. Such high dielectric constant implies high electrical dipole moment. In literature, there are not many measurements of these two quantities on different manganites and it is assumed that for other manganites also, these two values will be of the same order of magnitude. Then, it seems to be a fit case for applying the Debye relaxation theory which explains heat generation. But two questions remain to be answered: (1) how the fluctuation of spin initiated by the magnetic component of microwave field can be

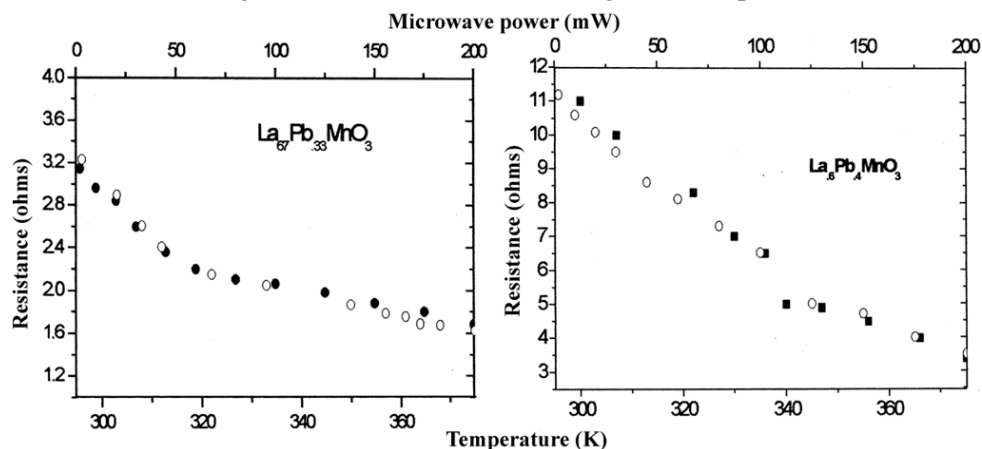


Fig. 3—Equivalence of direct heating and microwave heating by comparing resistances.  $R$  versus  $T$  by direct heating shown by solid circles and by microwave heating shown by hollow circles

transferred to rotational/orientational motion of a physical body and (2) what is the size of this physical body and what are its constituents? Regarding the first question, Brink *et al*<sup>14,18</sup>. argued that in lightly hole doped manganites, the holes at Mn<sup>4+</sup> sites are surrounded by the nearest neighbours Mn<sup>3+</sup> sites in which the occupied 3d orbitals have their lobes directed towards the central hole Mn<sup>4+</sup> site and with spins coupled ferromagnetically to the central spin. On examining the crystal structure of manganites it becomes clear that Mn<sup>3+</sup> sites are also surrounded by nearest neighbour Mn<sup>4+</sup> sites and their orbitals are directed towards the central Mn<sup>3+</sup> site. Thus there is a strong spin-orbital coupling. Further it is supported by Weibe *et al*<sup>19</sup>. who argued that since the transfer of electrons between different Mn-ions always proceeds via the completely filled shell of the bridging oxygen sites, the hopping matrix elements acquire a particular orbital dependence, which leads to spin-orbital interactions. Regarding the second question, it can be said that the physical body consists of the central Mn<sup>3+</sup> ion and its nearest neighbours which include Mn<sup>4+</sup> ions and also nearest La and alkaline earth ions and oxygen octahedra surrounding Mn-sites. Mn<sup>3+</sup> ions are surrounded by the nearest neighbour Mn<sup>4+</sup> ions and each Mn ion is surrounded by corner sharing octahedra of oxygen ions and La and alkaline earth ions occupy the center of the cube formed by the Mn sites. Thus these ions are interconnected. Again taking the structure of manganites to be cubic (for simplicity) of a side=3.86 Å, the space occupied by a particular Mn<sup>3+</sup> ion plus all its nearest neighbours is nearly a sphere whose diameter is ~11 Å. The e<sub>g</sub> electron of Mn<sup>3+</sup> ion trapped in oxygen octahedron is treated as a polaron. Polarons of different nature have been observed, for example, lattice polarons<sup>12,13,19</sup>, orbital polarons<sup>20</sup>, spin or magnetic polarons<sup>18,21</sup>. As there is strong interaction between lattice, orbital and spin degrees of freedom in manganites, the polaron can be viewed as combined orbital-spin-lattice polaron. The size of the polaron<sup>20,21</sup> has been given as 10 Å and 12Å which is nearly the same estimated by us.

There are many complexities in the behaviour of manganites, but this new aspect, i.e., heating of manganites by magnetic component of microwave

field had not been viewed earlier as no experiment had been done on the dependence of EPR spectra of manganites as a function of applied microwave power(as reported by us in the Ref. (15). This problem has been brought to light for the first time and perhaps answered satisfactorily.

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