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Transport properties and magnetic behaviour of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ single crystals

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Abstract. A semiconductor–metal transition occurring just below the Curie temperature T_C was observed in single crystals of perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for $x \geq 0.175$. For $x \leq 0.15$ the crystals exhibit only semiconducting behaviour. These transport properties are closely connected with the electron transfer mediated by the double exchange interaction between Mn^{3+} and Mn^{4+} ions. The electronic state of manganese in these mixed systems is well illustrated by ^{55}Mn nuclear magnetic resonance study. A maximum in the magnetoresistance (MR) was observed near T_C for the crystals with $x \geq 0.13$ whereas huge MR persists well below T_C for the $x = 0.10$ sample, which is probably due to a non-collinear spin configuration.

1. Introduction

The perovskite LaMnO_3 is an insulating layered antiferromagnet with a Néel temperature of 100 K. By replacing La^{3+} with a divalent cation (Ba, Ca or Sr) the mixed compounds $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ become ferromagnetic at room temperature for x in the range 0.2–0.4 [1, 2]. The creation of Mn^{4+} ions resulting from this substitution gives rise to ferromagnetism by the double exchange interaction [3–5] with neighbouring Mn^{3+} ions and also to metallic behaviour below the Curie temperature T_C . Recently colossal magnetoresistance (127 000% at 77 K and 1300% at 260 K) was reported for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ films [6]. Such a high value near room temperature makes the subject of mixed Mn oxides very attractive. In this paper we report on the investigation of the transport properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ single crystals with $0.1 \leq x \leq 0.35$. These properties are correlated with the magnetization data and the microscopic behaviour of Mn^{3+} and Mn^{4+} ions from NMR spin echo experiments. All the measurements were made on non-oriented single crystals.

2. Experimental procedure

Powder mixtures of lanthanum and strontium carbonates and manganese oxides were heated in air at 1100 °C for 3 d, sintered and then grown as single crystals by a floating zone method associated with an image furnace [7, 8]. This technique has proved well suited in the past to obtain single-crystalline or highly textured material [9].

The magnetization measurements were made using a home-made SQUID magnetometer. Electrical resistivity measurements were made by the standard four-probe technique, using

$2 \times 2 \times 9 \text{ mm}^3$ stripes up to 320 K. The ^{55}Mn NMR measurements were carried out at 4 K on crystals of cylindrical shape, using a variable-frequency spin echo apparatus. The interval between the exciting and refocusing rf pulses was about $3 \mu\text{s}$, which is an order of magnitude shorter than the nuclear transverse relaxation time.

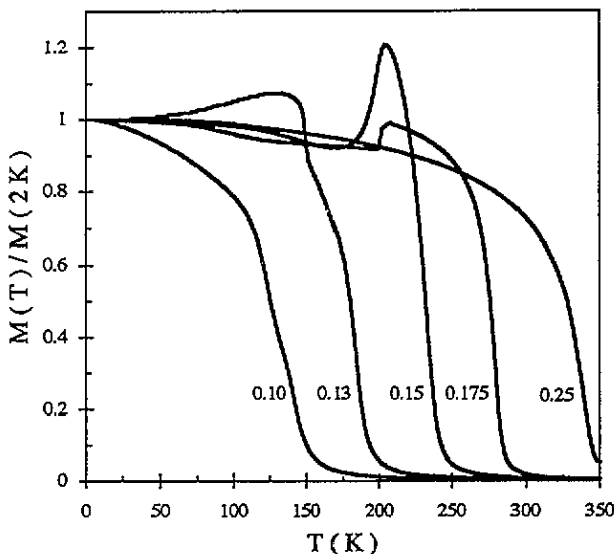


Figure 1. The temperature dependence of the magnetization at 0.1 T in single crystals of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. The x values are indicated.

3. Results and discussion

The magnetic properties of single crystals of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ are similar to those observed in polycrystalline samples [1] with the Curie temperatures T_C of the same order (figure 1). As the measurements were done at a rather low field yielding a sharp ferromagnetic transition the magnetization M is expected to depend on the magnetic anisotropy and on the relative field direction. The magnetic anisotropy in these Mn oxides would be uniaxial as found in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ oxides [10]. We have checked the dependence of the magnetization on the field direction on an $x = 0.10$ sample. The field was applied successively along the crystal growth direction (z) and two other perpendicular directions (x and y). The highest magnetization for the x direction reveals that this direction is closest to the easy axis (figure 2). It is interesting to note that the determination of T_C , which was our primary goal in this work, is practically independent of the field orientation. The resistivity measurements confirms the metallic behaviour for the $0.175 \leq x \leq 0.35$ crystals below T_C (figure 3) as do the results reported by Tokura *et al* [11]. The $x \leq 0.15$ crystals are semiconducting. The transport mechanism in the paramagnetic phase is probably governed by magnetic polaron hopping [12, 13] of activation type. The activation energy E could be measured for two crystals with relatively low Curie temperature (figure 4). The E value decreases with increasing Sr concentration like the variation in $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ compounds where the disappearance of E indicates a Mott transition [14]. The value reported for $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$

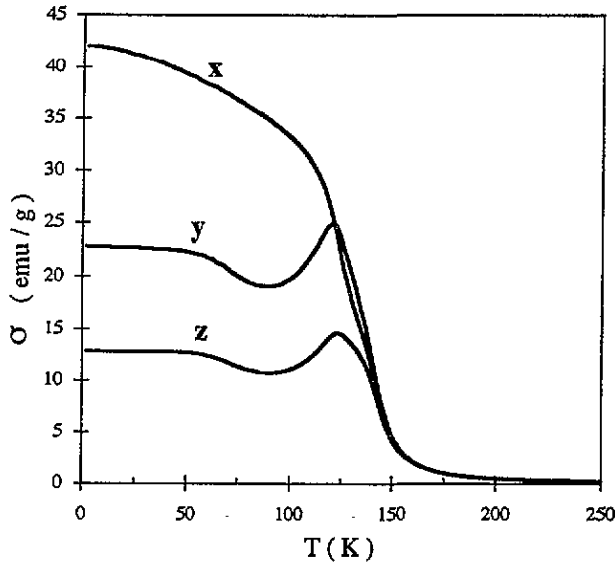


Figure 2. Magnetization as a function of temperature for the $\text{La}_{0.90}\text{Sr}_{0.10}\text{MnO}_3$ crystal in a dc magnetic field of 0.1 T along the crystal growth direction (z) and two other perpendicular directions (x and y) respectively.

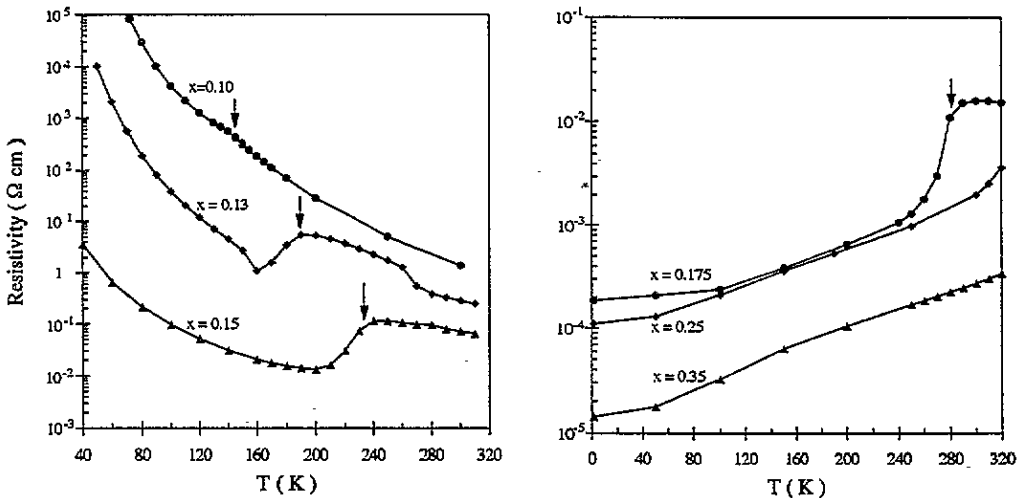


Figure 3. The temperature dependence of the resistivity in single crystals of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. The arrows indicate the Curie temperatures.

[13] after annealing is included in table 1 which confirms this trend. The anomaly presenting a jump in resistivity at 260 K for the $x = 0.13$ sample is ascribed to a structural transition like that observed at 370 K for the $x = 0.15$ sample [11].

The electrical conductivity in these oxides was explained in terms of double exchange interaction [3] with transfer of an electron from the e_g state of an Mn^{3+} ion to a vacant e_g state of an adjacent Mn^{4+} ion across an O^{2-} ion. Each Mn site is considered to have

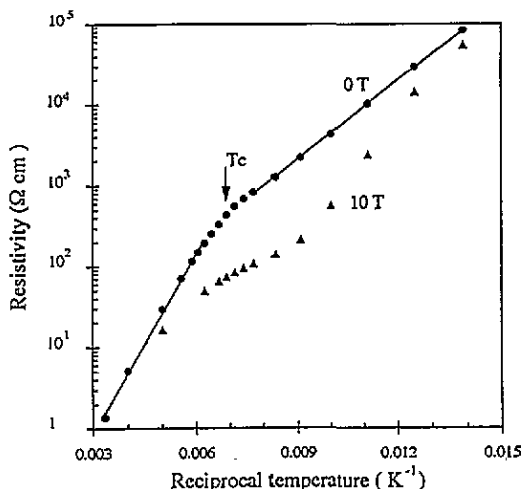


Figure 4. Resistivity versus reciprocal temperature for the single crystal of $\text{La}_{0.90}\text{Sr}_{0.10}\text{MnO}_3$.

Table 1. Activation energy E of an electron hopping in the paramagnetic phase of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ oxides.

x	0.1	0.13	0.16
E (meV)	146	113	70 [13]

a local spin $S = \frac{3}{2}$ resulting from three localized electrons in the t_{2g} state. The effective electron transfer [4] was shown to be proportional to $\cos(\theta/2)$ where θ is the relative angle between two neighbouring local spins. The electrical resistivity ρ is then a minimum when the spins are parallel. This mechanism gives rise to a negative magnetoresistance (MR) for a disordered spin system. The change due to a magnetic field in this spin disorder resistivity is expected to be largest at the Curie temperature T_C because the parallel susceptibility is a maximum at this point. At low temperatures the spins in Mn oxides with $x \geq 0.13$ are quasiparallel as revealed by the magnetization data [2]. As a consequence the magnetoresistance is a maximum near T_C and decreases at lower temperatures for the $x \geq 0.13$ crystals (figure 5). For the $x = 0.175$ crystal exhibiting a metallic behaviour a sharp MR cusp was observed just below T_C . For the $x \geq 0.25$ crystals with $T_C \geq 340$ K similar MR peaks are expected to occur above 320 K as one can guess from a strong decrease in magnetoresistance at lower temperature. The maximum MR value $(\rho_0 - \rho_H)/\rho_0$, where ρ_0 and ρ_H are the resistivities in zero field and in a field H respectively, is as high as 93% at 10 T for the $x = 0.13$ crystal. The MR values in these crystals are found to be higher than in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ films [15], which were assumed to have an oxygen excess.

For the $x = 0.1$ polycrystalline sample the saturation magnetization extrapolated to zero field is one-half of that of the ferromagnetic $x \geq 0.13$ samples [2], revealing a canted [5] or spiral magnetic structure [16]. Thus the observation of huge MR below the magnetic transition in a wide range of temperatures, unlike the previous cases, is explained by the forced alignment of spins in the field direction. Below 90 K the presence of an additional positive magnetoresistance ($\rho_{10\text{ T}} \sim 1.5\rho_{5\text{ T}}$), of which the origin is not clear, causes a drop in MR at low temperature. The resistivity could not be measured below 70 K because of its high value.

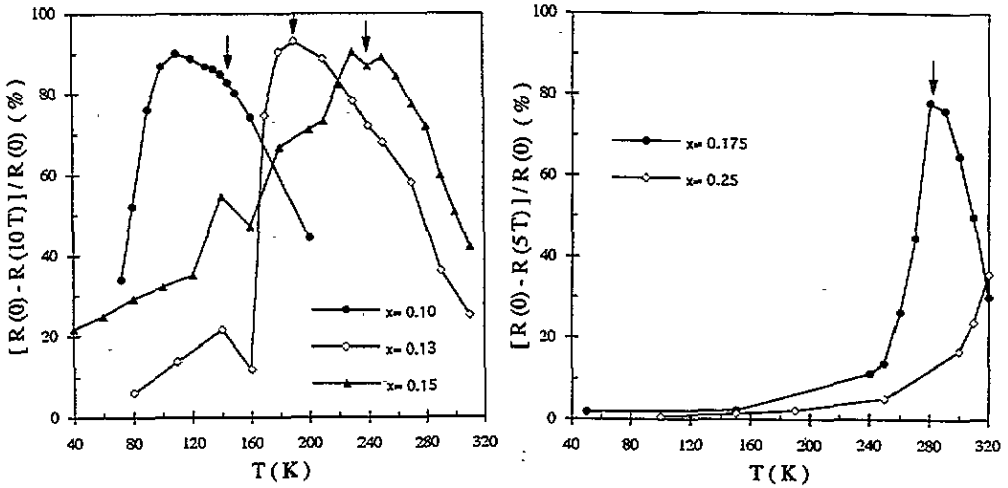


Figure 5. The temperature dependence of the magnetoresistance in single crystals at $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. The vertical arrows indicate the Curie temperatures. The data for the metallic samples are shown on the right.

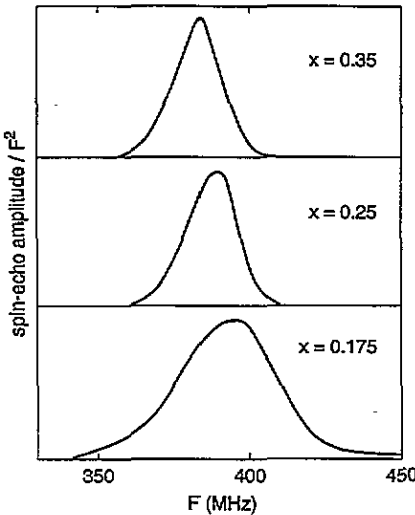


Figure 6. ^{55}Mn spin echo spectra at 4 K for the metallic $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ crystals with $x = 0.35$, 0.25 and 0.175.

The metallic ferromagnetism, which appears in the crystals with $x = 0.35$, $x = 0.25$ and $x = 0.175$, is best illustrated by ^{55}Mn NMR at 4 K (figure 6). If the rate at which an electron jumps from an Mn^{3+} ion to an adjacent Mn^{4+} ion is much higher than the resonance frequency, the Mn nuclei will experience a time-averaged hyperfine field of these ions, weighted by their relative concentration. This effect is known in magnetic resonance phenomena as motional narrowing. The ^{55}Mn resonance frequency arising from Mn^{4+} ions at octahedral sites in a polycrystalline Fe-Mn-Ni oxide is close to 325 MHz [17]. For Mn^{3+} ions at octahedral sites the hyperfine field is strongly anisotropic due to the spin dipolar

contribution of the $d_{x^2-y^2}$ ground state. As a result, a broad resonance spectrum centred at about 425 MHz was observed in this mixed oxide. For the present Mn oxides exhibiting metallic behaviour only one line at intermediate frequencies was detected. The spectrum is shifted to higher frequencies as the Sr concentration decreases, in accordance with the expected change in the relative concentration of Mn^{4+} ions. It may be noted that our results are rather different from those reported for polycrystalline $La_{1-x}Ca_xMnO_3$ samples [10]. For example, the polycrystalline sample with $x = 0.175$ exhibits, in addition to a broad spectrum in the range 360–420 MHz, a small peak (a few per cent in relative integrated intensity) centred at 323 MHz, arising from Mn^{4+} sites. This residual signal indicates that some regions of this sample are not conducting, due probably to inhomogeneities in composition. If the whole sample were semiconducting the intensity of the signal around 323 MHz would be of the order of $x = 17.5\%$. For the $x \leq 0.125$ polycrystalline samples no signal was observed in the range 350–450 MHz which was ascribed to short spin echo decay time. In contrast the NMR spectra observed in our crystals are complete and change coherently with Sr concentration.

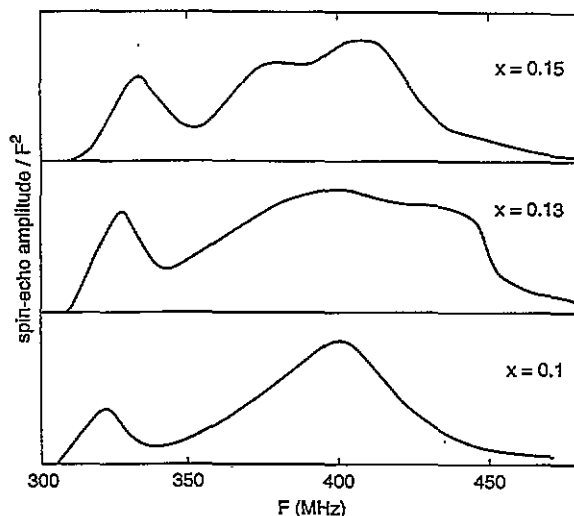


Figure 7. ^{55}Mn spin echo spectra at 4 K for the semiconducting $La_{1-x}Sr_xMnO_3$ crystals with $x = 0.15, 0.13$ and 0.1 .

When the Sr concentration is decreased to 0.15 the crystal exhibits a semiconducting behaviour at low temperatures. As a consequence the resonance spectrum is now composed of a sharp line at 333 MHz and a broad spectrum at higher frequencies (figure 7) associated with Mn^{4+} and Mn^{3+} sites respectively as observed in Fe–Mn–Ni oxides. Similar spectra were observed for the samples with lower Sr concentration and accordingly with a weaker signal from Mn^{4+} sites. For Mn^{4+} ions with t_{2g}^3 configuration, it can be shown that the singlet ground state [18] $|2^a\rangle$ of a 3F ion gives rise to zero spin dipolar hyperfine field. In this case the hyperfine field which arises mainly from the Fermi contact term is nearly isotropic, resulting in a sharp line. In contrast, the Mn^{3+} hyperfine field is very sensitive not only to the spin direction, but also to the local environment which determines the crystal field. For example, the $d_{x^2-y^2}$ orbital ground state of an Mn^{3+} ion in a tetragonal crystal field, due to the Jahn–Teller distortion, will mix with the $d_{3z^2-r^2}$ state in the presence of an

orthorhombic field. The Sr^{2+} and Mn^{4+} ions are expected to have a direct effect through their differing charge and an indirect effect via O^{2-} displacements on the crystal field of a neighbouring Mn^{3+} site, resulting finally in a distribution of the hyperfine field.

4. Conclusion

We have correlated the resistivity below the Curie temperature of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ single crystals with the microscopic properties of Mn^{3+} and Mn^{4+} ions. The metallic phase for the samples with $x \geq 0.17$ and the semiconducting phase for those with $x \leq 0.15$ are connected with the electron transfer between Mn^{3+} and Mn^{4+} ions as illustrated by the NMR results. The negative magnetoresistance is believed to be due to spin-dependent electron scattering, as the electron transfer is favoured by a parallel spin configuration. The present crystals exhibit large magnetoresistances which are higher than those found in Sr-doped LaMnO_3 film samples.

Acknowledgments

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References

- [1] Jonker G H and Van Santen J H 1950 *Physica* **16** 337
- [2] Jonker G H 1956 *Physica* **22** 707
- [3] Zener C 1951 *Phys. Rev.* **82** 403
- [4] Anderson P W and Hasegawa H 1955 *Phys. Rev.* **100** 675
- [5] de Gennes P G 1960 *Phys. Rev.* **118** 141
- [6] Jin S, Tiefel T H, McCormack M, Fastnacht R A, Ramesh R and Chen L H 1994 *Science* **264** 413
- [7] Revcolevschi A and Collongues R 1969 *C. R. Acad. Sci., Paris* **266** 1767
- [8] Revcolevschi A 1970 *Int. Hautes Temp.* **7** 73
- [9] Revcolevschi A and Dhalenne G 1993 *Adv. Mater.* **5** 657
- [10] Matsumoto G 1970 *J. Phys. Soc. Japan* **29** 615
- [11] Tokura Y, Urushibara A, Moritomo Y, Arima T, Asamitsu A, Kido G and Furukawa N 1994 *J. Phys. Soc. Japan* **63** 3931
- [12] Helmolt R V, Wecker J, Holzapfel B, Shultz L and Samwer K 1993 *Phys. Rev. Lett.* **71** 2331
- [13] Ju H L, Kwon C, Li Q, Greene R L and Venkatesan T 1994 *Appl. Phys. Lett.* **65** 2108
- [14] Mott N F 1972 *Adv. Phys.* **21** 785
- [15] Helmolt R V, Wecker J, Samwer K, Haupt L and Barner K 1994 *J. Appl. Phys.* **76** 6925
- [16] Inoue J and Maekawa S 1995 *Phys. Rev. Lett.* **74** 3407
- [17] Mizoguchi M and Tasaki A 1970 *J. Phys. Soc. Japan* **29** 1382
- [18] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon)