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First-order field-induced transition, magnetoresistance, and giant magnetostriction in single crystals of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$

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The well-established paraferromagnetic transition (T_c) accompanied by a semiconductor-metal transition in the bilayer manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ was found to be suppressed in single crystals of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$. However, a first-order field-induced transition was observed accompanied by a huge decrease of the *c*-axis resistance by a factor of one million. The magnetoresistance data correlate well with an equally large negative magnetostriction. In addition, strong anisotropic properties are observed. The data reflect the presence of unusual interplay among spin, charge, and orbital degrees of freedom in this layered structure.

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The discovery of a colossal magnetoresistance (CMR) effect followed by the observation of other interesting phenomena such as charge ordering, isotope effect, etc., in the Mn perovskites $Ln_{1-x}D_xMnO_3$ (Ln=rare earths; D=Ca, Sr, Ba, Pb) has stimulated further research into these fascinating group of materials.[1] Several models[1–5] based on the double exchange (DE) interaction, Jahn-Teller distortion, antiferromagnetic (AF) superexchange, charge-orbital ordering interaction, phase separation, etc., are presently proposed to account for some of the unusual properties observed. In parallel to the data relative to this group of compounds, interesting results have been reported on the $n=2$ compounds of the Ruddlesden-Popper series generally described as $(Ln_{1-x}D_x)_{n+1}Mn_nO_{3n+1}$. In the $n=2$ bilayer Mn perovskite, two MnO_6 layers are alternately stacked with $(Ln,D)_2O_2$ layers along the *c* axis of the structure whereas in the case of $Ln_{1-x}D_xMnO_3$, which is the $n=\infty$ term of the series, the MnO_6 octahedra extend all over the space. The reduced dimensionality of the $n=2$ compounds has been shown to have interesting consequences on their physical properties. Thus, the compound $La_{1.2}Sr_{1.8}Mn_2O_7$ exhibits[6] a paramagnetic-to-ferromagnetic transition (PFT) at $T_c \sim 125$ K, accompanied by a semiconductor to metal transition (SMT) and the CMR reaches 98% near T_c. Further, in this compound, there is a possibility of interplay between hybridization and chemical potential. At room temperature, the Mn-O bonds are found to be longer in the *z* direction than in the *x*-*y* plane.[7] This would imply occupation of the $3d_{z^2-r^2}$ orbital while the hybridization would favor the occupation of the $3d_{x^2-y^2}$ one. This would affect the magnetic, transport and magnetoelastic properties as was also pointed out by Kimura *et al.*[8] in their studies wherein they varied the nominal hole concentration *x* between 0.3 and 0.45 in $La_{2-2x}Sr_{1+2x}Mn_2O_7$. We have, in contrast, kept the hole density constant at $x=0.4$ and investigated the effect of the ionic radius at the rare-earth site on the physical properties of $(La_{1-z}Pr_z)_{1.2}Sr_{1.8}Mn_2O_7$ compounds.

We have found recently[9,10] that for Pr($z=0.2$), T_c decreases from 125 to 98 K, this change being accompanied by a SMT at 98 K and that the magnitude and sign of the lattice striction were strongly affected. As we further increased the *z* concentration of Pr to 0.6, we noted that the spontaneous magnetic order was absent but found a field-induced first-order PFT accompanied by a dramatic decrease in resistance by a factor of one million. This huge magnetoresistance (MR), measured with current and magnetic field parallel to the *c* axis, was correlated with an equally large magnetostriction (MS).

We present here detailed magnetization (*M*), resistivity (ρ), MR and MS studies as a function of magnetic field and temperature, carried out in both the *ab* plane and along the *c* axis of a $z=0.6$ single crystal. Our results demonstrate the presence of unusual interplay among the spin, charge, and orbital degrees of freedom in this layered structure.

Single crystals of $(La_{1-z}Pr_z)_{1.2}Sr_{1.8}Mn_2O_7$, with $z=0.6$, were grown from sintered rods of same nominal composition by the floating-zone method using a mirror furnace. Crystals could be cleaved, yielding to shiny surfaces. X-ray Laüe patterns have indicated the cleaved surface to be the ab plane with, therefore, the *c* axis perpendicular to it. The x-ray powder pattern obtained by crushing part of the cleaved crystal did not indicate the presence of any additional phases and the lattice parameters were calculated to be $a=3.863$ Å and $c=20.150$ Å. Thus, the substitution by Pr has resulted in a small contraction of the *a* parameter and an expansion of the *c* parameter since, for $z=0$, we found $a=3.875$ Å and $c=20.13$ Å. This will have important consequences on the magnetic anisotropy, magnetization, CMR and magnetostriction, as will be shown below. The composition of the cleaved surface of the sample, as revealed by energy-dispersive x-ray analysis, was very close to that of the starting rods. The dimensions of the crystals for the ρ and MS experiments were typically 3.4×2.8 mm^2 in the *ab* plane and 1 mm along the *c* axis. A commercial SQUID (Quantum Design) magnetometer was used to measure *M*, ρ, and MR, as a function of temperature and field. Four sputtered gold pads with silver paste and indium wires were used for electrical contacts. For resistivity measurements with $I\parallel$ to the *c* axis, ring type contacts on both sides of the crystal platelet were used, as described by Kimura *et al.*[8] The thermal expansion in the *ab*

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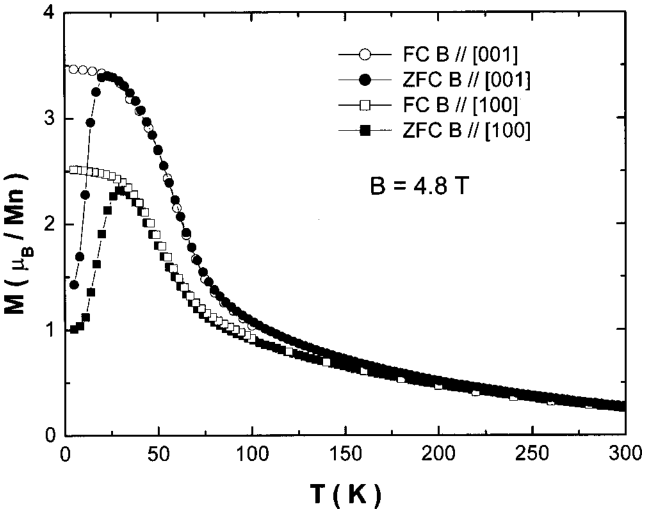

FIG. 1. ZFC and FC magnetization (M) as a function of temperature in a field of 4.8 T with $B\|[001]$ and [100].

plane and along the c axis were measured by means of a conventional strain gauge technique using a Gifford-McMohan-type helium refrigerator. Magnetostriction in fields higher than 5 T were carried out at the High Field Laboratory of Tohoku University.

Field-cooled (FC) and zero-field-cooled (ZFC) magnetization ($B\|ab$ and c) of a fraction of the single crystal, as a function of temperature, are shown Fig. 1. The ZFC magnetization increased strongly as T decreased below 100 K but decreased starting from 28 K, even in a field of 5 T. The FC data differed strongly from the ZFC data for $T<28\,\mathrm{K}$ and did not show any decrease at 28 K. This possibly indicates the presence of a spin-glass-like state or to the coexistence of antiferromagnetic and ferromagnetic clusters. The data further indicated that the magnetization anisotropy M_{ab}/M_c had decreased considerably due to the Pr substitution from about 6–8 to less than 1. In Fig. 2 are shown M vs B($\|$ab plane and to c axis) data at selected temperatures. The most important observation which can be made is the first-order transition at 15 K with $B\|[001]$ at about 3 T. This transition at 15 K, due to strong anisotropy, takes place at a higher field value of 4 T when $B\|$ab. Whereas the c-axis magnetization at 15 K showed a large hysteresis, the in-plane data did not show any. For $T>50\,\mathrm{K}$, both the out of plane and in-plane magnetization data were reversible.

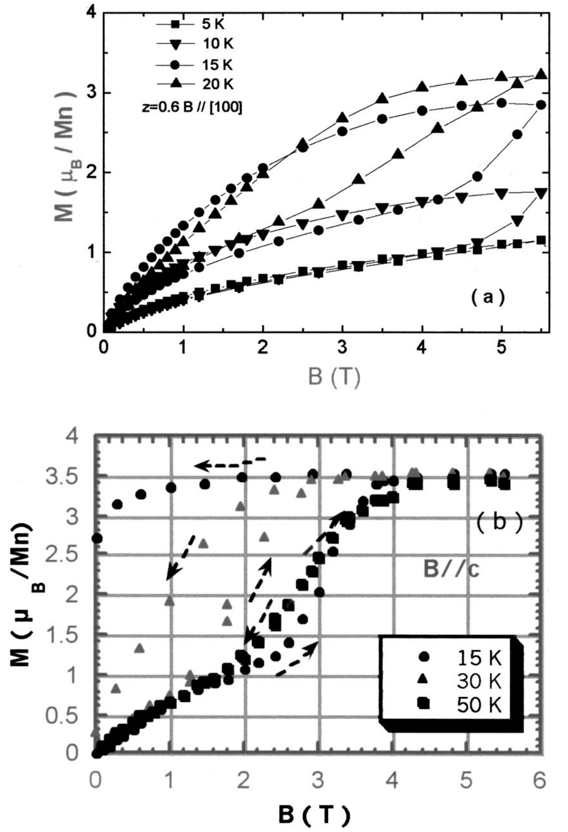

FIG. 2. M as a function of B at selected temperatures with (a) $B\|[100]$ and (b) $B\|c$ axis.

Now, let us consider the transport properties. In the absence of any applied field, ρ showed a semiconductorlike behavior as T decreased both with $I\|a$ and $I\|c$ (Fig. 3). An anisotropy amounting to $\rho_c/\rho_a=60$ was observed at 300 K and increased dramatically to 2×10^5 as T decreased to 5 K. Note that in the case of the unsubstituted compound,[5] this ratio was equal to 100 reflecting a very strong lattice effect on the anisotropy. Further, a field-induced SMT was observed. The maximum in the resistivity that was found at 75 K, in the case of $I\|B\|[110]$, was shifted to a higher temperature (100 K) for $I\|B\|[001]$. The huge negative magnetoresistance is best illustrated in Figs. 4(a)–4(c) where the resistance (R) of the sample, as a function of B at selected temperatures, is shown. Notice a close relation between R and M as a function of B for a given T. The protocol for these measurements, for each T, was the following: first, the sample was heated to 300 K, cooled to temperature T, and the data taken by increasing the field. For $I\|B\|[110]$ at 10 K, MR hardly changed for $B<5$ T but decreased by a factor of 5 at $B=5.5\,\mathrm{T}$. A sizeable hysteresis was observed when B was decreased to zero. At 25 K, R started decreasing for $B\sim3.5\,\mathrm{T}$ and resulted in a large decrease by a factor of 2000 as B was increased to 4 T. A large hysteresis was observed

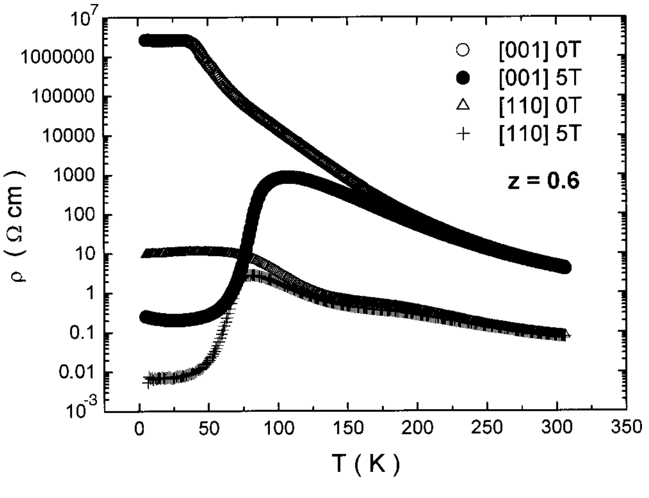

FIG. 3. Resistivity as function of temperature in zero and in a field of $B=5$ T for with $I\|[001]\|B$ and $I\|[100]\|B$.

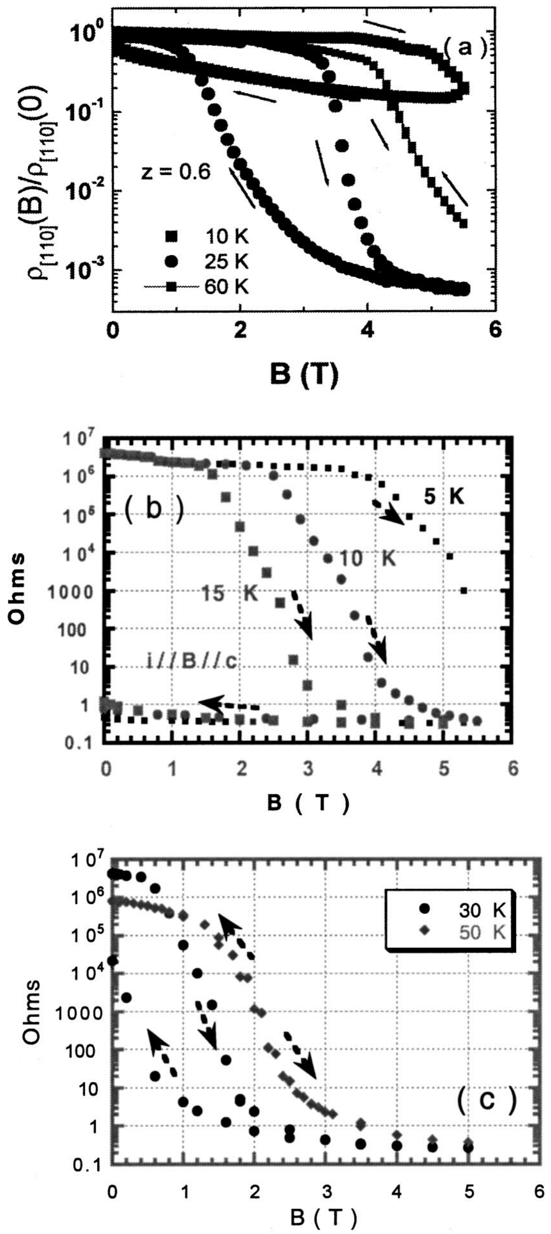

FIG. 4. (a) Normalized resistivity as a function of B with $I \| B \| [110]$ at selected temperatures (b), (c) Resistance as a function of B with $I \| B \| [001]$ at selected temperatures.

but the MR was zero for $B=0$. For $T=60\,\mathrm{K}$, the MR was still large but no hysteresis was observed. The curves were symmetrical on field reversal.

The data obtained for $I \| [001] \| B$ are quite dramatic and are very different from what is described above. At 5 K, for $B>4$ T, R decreased rapidly and the value of MR reached a huge value of one million. A large hysteresis was observed as B was decreased to zero and the sample retained the low R value, even when the field direction was reversed and then switched off. One had to wait for hours before R increased. The relaxation studies will be reported elsewhere. For $10 < T < 50\,\mathrm{K}$, a huge decrease in R was found to occur at lower fields, accompanied by a hysteresis. For $T \geqslant 50\,\mathrm{K}$, no hysteresis was observed.

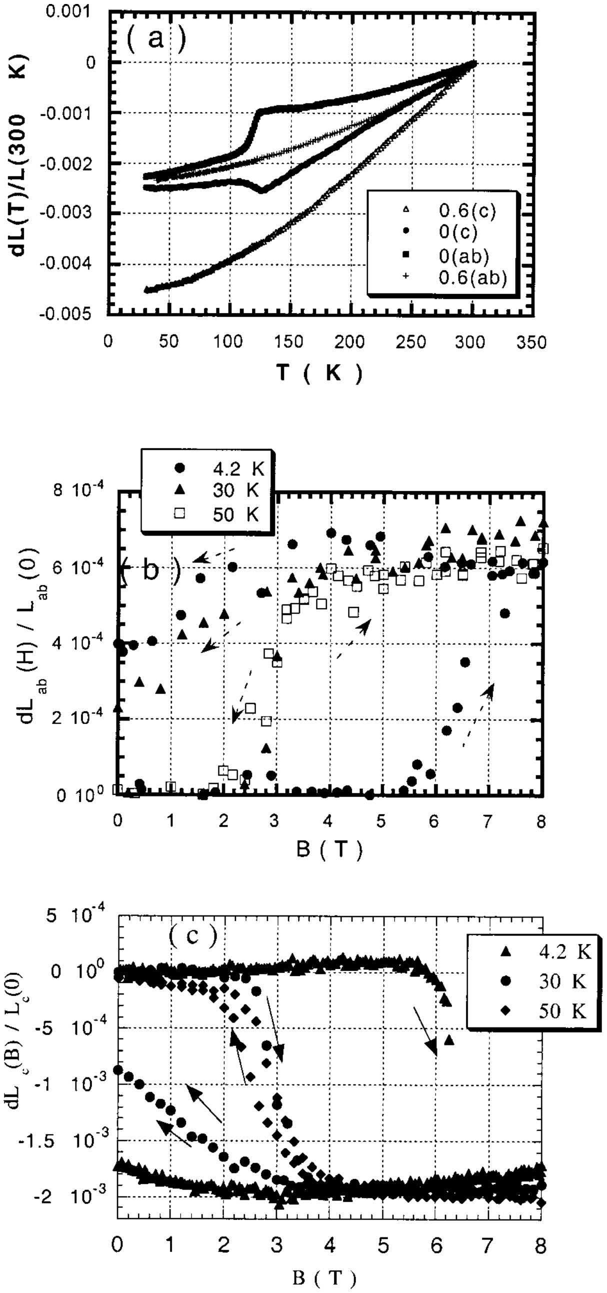

FIG. 5. (a) $dL(T)/L(300\,\mathrm{K})$ as a function of temperature measured along the ab plane and along the c axis for two concentrations of Pr, $z=0$ and 0.6. (b) The ab-plane magnetostriction as a function of field at selected temperatures for $z=0.6$, (c) The c-axis magnetostriction as a function of field at selected temperatures for $z=0.6$.

Let us discuss now the striction as a function of temperature and magnetostriction (MS) at selected temperatures, as a function of B, which have a strong bearing on MR effects [Figs. 5(a)–5(c)]. The data for $z=0$ are taken from Ogasawara *et al.*[9] The sample with $z=0.6$ did not show any anomalies as was seen for $z=0$ near 120 K indicating the absence of any spontaneous order in the present compound. However, we note that the striction for this sample, especially along the c axis, was quite large and negative at all temperatures. The MS data show quite interesting features.

At 4.2 K, the MS (along the *c* axis) remained constant as a function of B until 5 T and suddenly showed a very large decrease for $B > 6$ T. As the field was reduced to zero, a large hysteresis was observed. As T was increased to 30 and 50 K, the change in the magnitude of MS remained the same but the decrease occurred at lower fields and the width of the transition decreased considerably very similar to the *c*-axis resistivity vs B data. The MS in the ab plane also showed a hysteresis but it was positive and about 4 times smaller.

We will discuss now qualitatively our findings considering data reported on similar compounds and available models.[1–5] The occurrence of a first-order PFT transition accompanied by a similar first-order transition in MR and MS is not so common. The field-induced PFT (Ref. 12) as well as the volume striction,[13] showing hysteretic effects that were observed[12] in $Pr_{1-x}Ca_xMnO_3$, were attributed to a melting of the insulating charge-ordered state. However, in our compound, no charge ordering effects seem to be present.

Let us compare our data to those reported on the Nd-substituted ($z = 0.4$) compound by Moritomo *et al.*,[11] and on the $x = 0.45$ hole doped compound by Kimura *et al.*[8] Note, however, that for the Nd-substituted samples, neither *c*-axis MR nor MS were reported. The $x = 0.45$ sample is selected for comparison because of a similar semiconductor behavior in the absence of field. The M vs T and the M vs B data of our sample resemble very much those reported for the Nd-substituted samples and possibly indicates the presence of spin clusters or magnetic domains consisting of Mn^{3+} and Mn^{4+} with well localized e_g electrons, leading to an insulating ground state. The striction data of the $x = 0.45$ sample resemble very much those found for our sample. For the in-plane FM interaction to be effective, as in the case of the $x = 0.4$ sample, the a parameter should have an optimum value[8] and thus our sample should show an increase in striction upon cooling. However, what we observed was a decrease and hence no spontaneous magnetic order could be expected. At 10 K, as B increased from zero, for $I \| B \| c$ axis, though M increased rapidly, ρ did not show any change, even though the clusters or domains might have been partially aligned. Nor was there any change in MS. It was only when the sample was fully magnetized that ρ showed a rapid decrease by a factor of one million, accompanied by a considerable decrease in MS. Whereas the percolation/phase separation model as well as the double exchange mechanism can account for the observed SMT and the MR, an explanation of the MS is hard to come by.

Let us look at the resistivity data reported on the $x = 0.45$ sample in comparison with those presented here. In both cases, there is an absence of SMT for $B = 0$ but a field-induced transition was observed. The resistivity anisotropy (at 5 K) and the *c*-axis MR were larger by a factor of 200 and 20, respectively, in our sample. Further, whereas our sample exhibited respectively negative and positive values of $dL_c(5T)/L_c(0)$ and $dL_a(5T)/L_a(0)$ at $\sim$5 K, the $x = 0.45$ sample showed an exactly opposite behavior. However, we suggest that the mechanism involved in both these cases should be the same and related to the mixing of the two orbital states $3d_{x^2-y^2}$ and $3d_{z^2-r^2}$. The various field-induced properties observed should result from changes in the orbital occupancy of the e_g electron.[8] It is interesting that an attempt was made recently to study theoretically the phase diagram of the double-layered perovskite taking into account orbital degeneracy, the strong Coulomb repulsion, and coupling with the lattice deformation.[14] An extension to the present system should be rewarding.

In summary, we have observed a field-induced first-order para to ferromagnetic transition accompanied by a huge *c*-axis resistance decrease of one million and a giant negative magnetostriction in the single crystals of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$. The data can be understood qualitatively as resulting from an interplay between charge and orbital degrees of freedom accentuated by lattice disorder and anisotropy induced by Pr substitution and the layered structure of the compound. Several interesting questions related to the nature of the ferromagnetic ground state and relaxation effects have to be answered before a complete understanding can be reached. Our data further point out the possibility of finely tuning several unusual properties by proper substitution in this quasi-two-dimensional compound.

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