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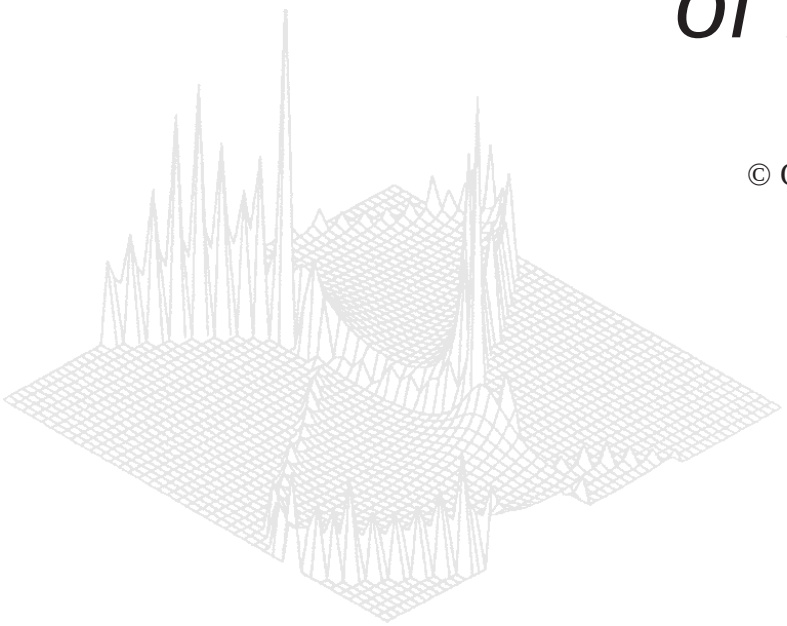

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High-field Study of Layered Manganites $R_{1/2}Sr_{3/2}MnO_4$ (R = La and Nd)*

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Abstract

We have studied the effects of a magnetic field on the magnetism and transport properties of the layered manganites $R_{1/2}Sr_{3/2}MnO_4$ (R = La and Nd) in pulsed magnetic fields up to 40 T. The R = La crystal shows metamagnetic-like transitions above 30 T, concomitantly with a colossal magnetoresistance (CMR) effect as large as $[\rho(0) - \rho(H)]/\rho(H) > 10^3$ with a field of $\mu_0 H = 38$ T at low temperatures. These transitions can be ascribed to the field-induced melting of the real-space ordering of the e_g electrons (charge ordering). For the R = Nd crystal, a magnetic field along the c-axis enhances the two-dimensionality in the conductivity. Moreover, we observed metamagnetic-like transitions accompanied by the CMR effects at low temperatures, in spite of the absence of charge ordering.

1. Introduction

In manganites of the Ruddlesden–Popper series, $(R_{1-x}M_x)_{n+1}Mn_nO_{3n+1}$ (R = a rare-earth element, M = Ba, Sr and Ca), an interplay among spin, charge and orbital (lattice) gives rise to various intriguing phenomena, such as the real-space ordering of e_g electrons (CO; charge ordering). The CO phenomenon is accompanied by a collective Jahn–Teller distortion which stabilises the ordering of the e_g orbitals (orbital ordering). As for the layered manganites (n = 1), the occurrence of CO in $La_{1/2}Sr_{3/2}MnO_4$ was demonstrated experimentally by measurements of the resistivity and susceptibility (Moritomo *et al.* 1995), electron diffraction (Bao *et al.* 1996) and neutron diffraction (Sternlieb *et al.* 1996) below 217–30 K. Recently, Murakami *et al.* directly observed the existence of $3x^2-r^2/3y^2-r^2$ type (or y^2-z^2/z^2-x^2 type) orbital ordering in $La_{1/2}Sr_{3/2}MnO_4$, concomitantly with CO, by means of an X-ray study (Murakami *et al.* 1998). In $La_{1/2}Sr_{3/2}MnO_4$, a substitution for La ions by smaller Nd ions decreases the CO transition temperature T_{CO}. No manifestations of CO have been observed for $Nd_{1/2}Sr_{3/2}MnO_4$ by measurements of the susceptibility down to 5 K (Moritomo *et al.* 1997) and also of the specific heat down to 0·6 K (Tokunaga *et al.* 1999, unpublished). A reduction of the average ionic radius for the R ions stretches

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the MnO_6 octahedra along the c-axis and stabilises the $3z^2 - r^2$ type character in the e_g orbitals. Therefore, this deformation of the MnO_6 octahedra seems to be incompatible with the $3x^2 - r^2/3y^2 - r^2$ type (or $y^2 - z^2/z^2 - x^2$ type) orbital ordering.

In the $n = \infty$ manganites, the application of magnetic fields significantly modifies the transport properties and structure through the interplay among spin, charge and orbital (lattice). For the $n = 1$ manganites, however, the effects of the magnetic field are less studied because high magnetic fields are needed. We have carried out measurements of the magnetisation and magnetoresistance for crystals of $R_{1/2}Sr_{3/2}MnO_4$ ($R =$ La and Nd) in pulsed magnetic fields up to 40 T. For the $La_{1/2}Sr_{3/2}MnO_4$ crystals, the magnetisation curves show metamagnetic-like behaviour below T_{CO}, accompanied by colossal magnetoresistance (CMR) effects, which can be regarded as the field-induced melting of the CO. On the other hand, magnetisation curves for $Nd_{1/2}Sr_{3/2}MnO_4$ also show metamagnetic-like behaviour at low temperatures, whereas the absence of CO has been reported (Moritomo *et al.* 1997). These metamagnetic-like transitions in $Nd_{1/2}Sr_{3/2}MnO_4$ are accompanied by CMR effects. In this paper, we show the results of the high-field magnetisation and magnetoresistance, and discuss the effect of magnetic fields on both layered manganites.

2. Experimental

A stoichiometric mixture of La_2O_3 (or Nd_2O_3), $SrCO_3$ and Mn_3O_4 was ground and calcined twice at 1300°C for 20 h. Then, the resulting powder was pressed into a rod and sintered at 1350°C for 30 h. Crystals of $La_{1/2}Sr_{3/2}MnO_4$ (LSMO) and $Nd_{1/2}Sr_{3/2}MnO_4$ (NSMO) were synthesised by the floating zone method as described previously (Moritomo *et al.* 1995).

Pulsed magnetic fields up to 40 T were generated for pulse duration times of 8–20 ms utilising a non-destructive long-pulse magnet with a capacitor bank of 300 kJ maximum accumulation energy (Takeyama *et al.* 1992). The magnetisation M was measured by means of an induction method by employing a pair of co-axial pick-up coils (Yamada *et al.* 1986). The voltage induced in the pick-up coils was recorded by a transient recorder with a sampling time of 10 μs and integrated numerically to obtain the magnetisation value. The magnetoresistance MR was measured by the standard dc four-probe method. In the present work, magnetic fields were applied along the c-axis of the crystal for all experiments.

3. Results and Discussion

Fig. 1 shows the magnetisation M of an LSMO crystal as a function of magnetic field H up to 38 T at various temperatures from 4 to 217 K. For each curve in Fig. 1, the origin is shifted vertically for clarity. At 4 K, the value of M increases steeply at around 35 T with an increasing field, and decreases with a large hysteresis between the field-increasing and field-decreasing process. This metamagnetic-like behaviour with a hysteresis is characteristic of a phase transition of the first order. The magnetisation reaches $3{\cdot}6$ μ_B at 38 T which is almost the same as the saturation moment of an average Mn ion moment ($3{\cdot}5$ μ_B). In Fig. 1, the solid and open triangles denote the inflection points of the M–H curves in the field-increasing and field-decreasing process respectively. As the temperature increases, the hysteresis of the M–H curve becomes smaller and

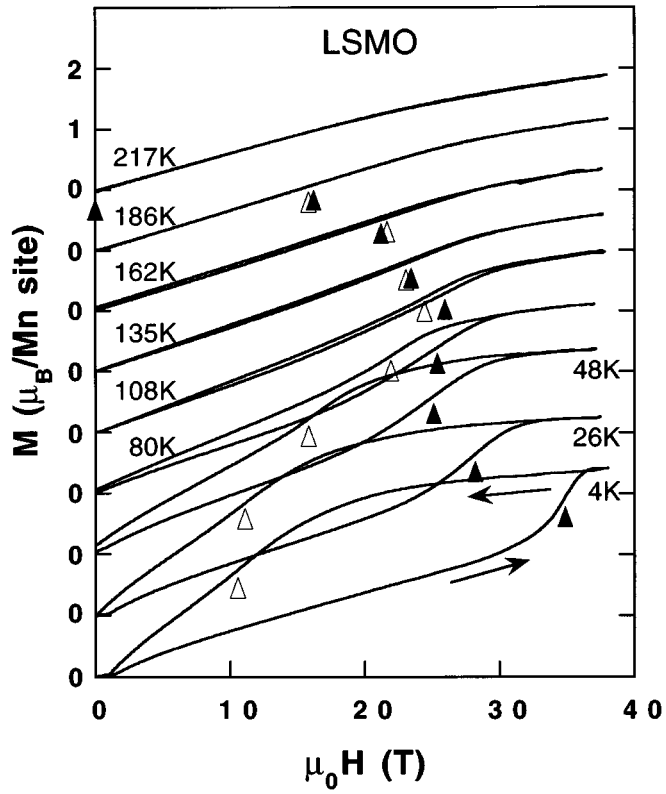

Fig. 1. Magnetisation of an LSMO crystal with pulsed-field up to 38 T along the *c*-axis. Solid and open triangles denote the inflection points of the *M*–*H* curves in the field-increasing and field-decreasing process respectively.

is hardly seen above 135 K. Since the inflection point is observed at a certain field, we can assign the field-induced transition below 217 K. This transition is considered to be of second order between 135 and 217 K, and of first order below 108 K. According to neutron diffraction measurements (Sternlieb *et al.* 1996), the Néel temperature of the LSMO is 110 K. A change of the transition from second to first order by decreasing the temperature, is perhaps related to the three-dimensional ordering of the Mn spins.

We have measured the magnetoresistance of an LSMO crystal with a current in the *ab*-plane (transverse magnetoresistance). Fig. 2 shows the in-plane resistivity ρ_{ab} versus magnetic field at temperatures from 108 to 240 K. The MR ratio $r_{\mathrm{MR}}(H) \equiv [\rho(0) - \rho(H)]/\rho(H)$ with a field of $\mu_0 H = 38$ T is equal to $1 \cdot 9$ at 240 K. A decrease in temperature increases $r_{\mathrm{MR}}(H)$ drastically up to more than 10^3 below 108 K. Such CMR effects accompanied by the metamagnetic-like transitions remind us of the field-induced melting of the CO, as observed in manganites with the $GdFeO_3$-type ($n = \infty$) structure (e.g. Kuwahara *et al.* 1995). We ascribe the field-induced transitions in LSMO to the collapse of the CO.

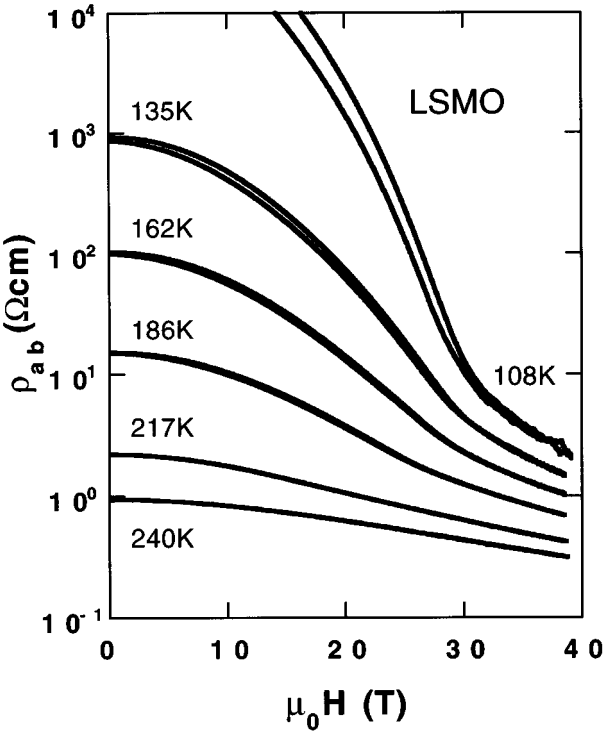

Fig. 2. Transverse magnetoresistance of an LSMO crystal with a dc current in the *ab*-plane. Magnetic fields of 38 T along the *c*-axis cause a CMR effect as large as $r_{\mathrm{MR}}(H) > 10^3$ below 108 K (see text).

We have also studied high-field magnetisation and magnetoresistance for NSMO crystals. Since no manifestations of CO have been observed for NSMO in measurements of the susceptibility and specific heat, we cannot expect any field-induced transition due to the melting of the CO at least above 0·6 K. The M–H curves for an NSMO crystal are plotted in Fig. 3. Above 105 K, the magnetisation moderately changes with a magnetic field up to 32 T. As the temperature decreases, hysteresis appears in the M–H curves. At 4 K, the value of M steeply increases above 23 T with a prominent hysteresis. This magnetic behaviour should be regarded as a field-induced phase transition. Taking into account the absence of CO, these transitions in NSMO are different phenomena from the melting of CO.

In addition to the magnetisation process, anomalous behaviour appears in the measurements of the magnetoresistance. Fig. 4 shows the transverse magnetoresistance for an NSMO crystal with a dc current in the *ab*-plane. As is clearly seen in Fig. 4, the magnetic field significantly affects the transport properties for NSMO, similar to that for LSMO. At 105 K, the MR ratio $r_{\mathrm{MR}}(H)$ reaches values as large as $1{\cdot}0 \times 10^3$ for a field of $\mu_0 H = 30$ T. At 48 K, the ρ_{ab}–H curve changes its slope at around 22 T. The slope of the M–H curve changes also at the same field. However, the slope of the ρ_{ab}–H curve becomes steeper above 22 T, whereas that of the M–H curve becomes less steep. This result implies that a simple consideration for the

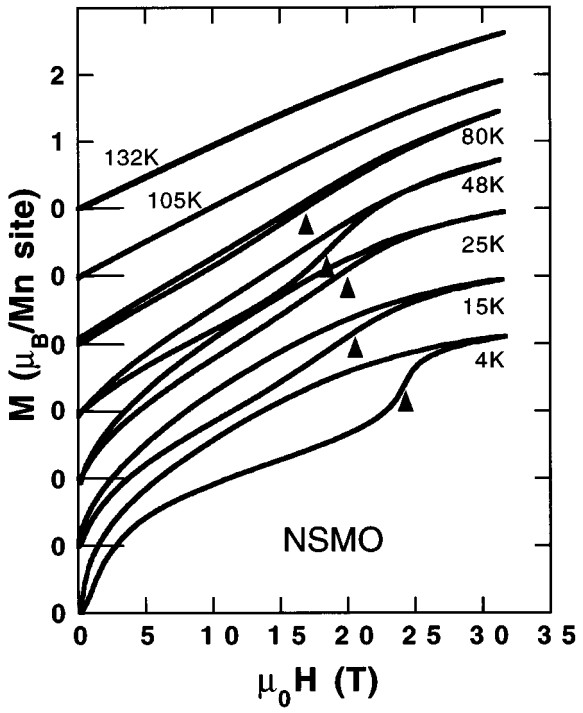

Fig. 3. Magnetisation process of an NSMO crystal at temperatures from 4 to 132 K. Above 105 K, the magnetisation increases gradually as H increases up to 32 T and decreases without any hysteresis. As the temperature decreases below 80 K, hysteresis appears in the M–H curve. Consequently, a metamagnetic-like steep increase in M can be observed at 4 K above 23 T.

effect of the reduction of spin scattering by an external field cannot explain the CMR effect in NSMO. In addition to the Hund rule coupling between the t_{2g} spins and the e_g electrons, other interactions should play an important role in NSMO.

To study this anomalous magnetic field dependence, we measured the resistivity with a current along the c-axis (ρ_c). Fig. 5a shows the ρ_c versus H curve at 48, 80 and 105 K. As is seen in Fig. 5a, ρ_c shows a negative magnetoresistance effect. Unfortunately, we cannot obtain the whole ρ_c–H curve below 80 K due to a limit in the dynamic range of the present measuring system. At 105 K, we have a value of $r_{\mathrm{MR}}(H) = 17$ for ρ_c at 30 T, whereas $r_{\mathrm{MR}}(H) = 1{\cdot}0 \times 10^3$ for ρ_{ab}. The quantitative difference in $r_{\mathrm{MR}}(H)$ is clearly demonstrated in the ρ_c/ρ_{ab}–H curve in Fig. 5b. Application of a magnetic field of 30 T increases ρ_c/ρ_{ab} by about two orders of magnitude. The result clearly shows enhancement of the two-dimensionality by a magnetic field. This effect is in the opposite direction to the effect of carrier localisation due to the cyclotron motion. In the following, we discuss the effect of the magnetic field on the $n = 1$ manganites taking into account the coupling between spin and orbital.

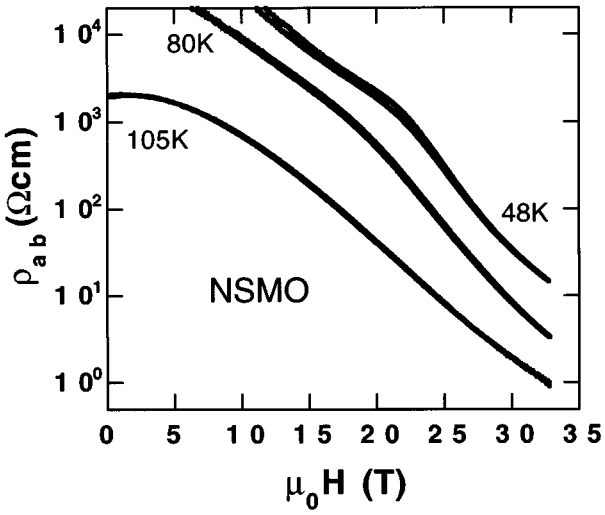

Fig. 4. Transverse magnetoresistance of an NSMO crystal at 48, 80 and 105 K. As is seen in the ρ_{ab}–H curve at 105 K, the MR ratio is $r_{\mathrm{MR}}(H) = 1{\cdot}0 \times 10^3$ at 30 T. In the ρ_{ab}–H curve for $T = 48$ K, the slope becomes steeper above 22 T.

For the $3d^4$ electronic configuration in a cubic crystal field (such as for Mn^{3+} in an MnO_6 octahedron), the e_g electrons have a degree of freedom on occupation of the twofold degenerate e_g orbitals. Although such a magnetic ion is Jahn–Teller active, deformation of the lattice is not determined uniquely unless we consider the interaction with the other octahedra; that is, the so-called orbital degrees of freedom. The transfer integral of the e_g electrons between the neighbouring sites (t_{ij}) reflects the anisotropy of the e_g orbitals. Due to the Hund rule coupling between the t_{2g} spins and e_g electrons, the e_g electrons tend to extend in the same magnetic sublattice. Therefore, the charge-extended-type of antiferromagnetic spin ordering (e.g. Wollan and Koehler 1955) favours the $3x^2 - r^2/3y^2 - r^2$ type orbital ordering, as is indeed suggested by a X-ray study of LSMO (Murakami *et al.* 1998). Application of the magnetic field aligns the t_{2g} spins and unifies the magnetic sublattices. In the forced-ferromagnetic state, the $3x^2 - r^2/3y^2 - r^2$ type orbital ordering loses its advantage so that orbital ordering in LSMO, and hence the CO, disappears by application of a magnetic field. In the case of NSMO, judging from the distortion of MnO_6-octahedra, the $3z^2 - r^2$ character can be dominant at zero magnetic field. According to the double-exchange theory (Anderson and Hasegawa 1955), the effective transfer integral of the e_g electrons between the neighbouring sites is reduced by a factor of $\cos(\theta/2)$ when $\theta \neq 0$, where θ denotes the relative angle of the neighbouring t_{2g} spins. Application of a magnetic field reduces θ and enhances the importance of the transfer energy. On account of the layered structure of the $n = 1$ manganites, the transfer energy in the ab-plane should be more important than that along the c-axis. Since the $3z^2 - r^2$ orbital extends along the c-axis, t_{ij} in the ab-plane between the $3z^2 - r^2$ states is as small as 1/3 of that between the $x^2 - y^2$ states. Thus, the application of a magnetic field may make the $3z^2 - r^2$ states unstable. If the $3z^2 - r^2$ character

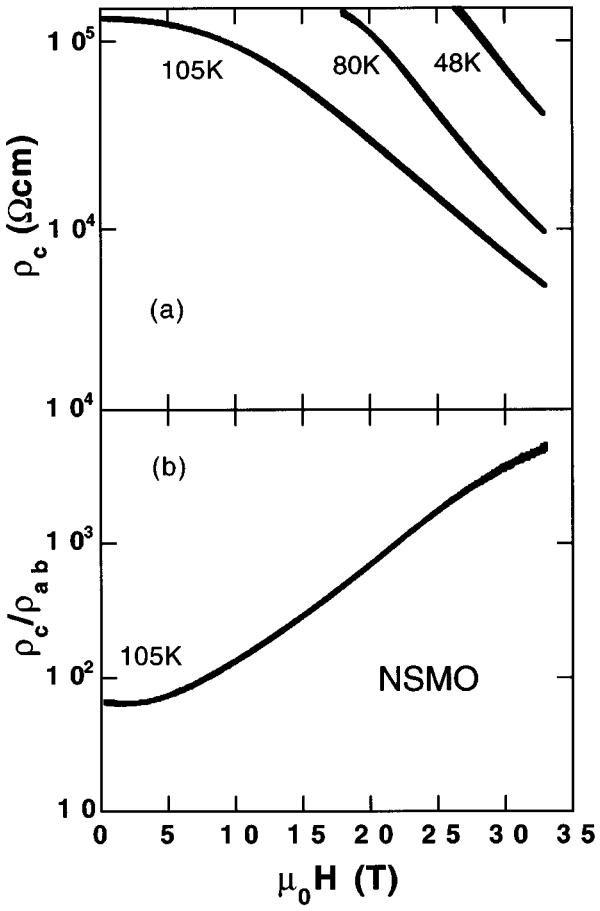

Fig. 5. (*a*) Longitudinal magnetoresistance of an NSMO crystal at 48, 80 and 105 K with magnetic field along the *c*-axis. Here $r_{\mathrm{MR}}(H) = 17$ at 105 K in a magnetic field of $\mu_0 H = 30$ T. (*b*) The magnetic field dependence of ρ_{ab}/ρ_c shows that the two-dimensionality of NSMO increases with magnetic field.

decreases, the two-dimensionality of the conductivity becomes more prominent. The observed enhancement of the two-dimensionality implies a reduction of the $3z^2 - r^2$ type orbital character. Since the orbital couples to the lattice through the Jahn–Teller distortion, a change of the orbital state may affect the crystal structure. This is one of the possible origins for the field-induced transitions in NSMO at low temperatures. However, we cannot neglect other effects, such as the existence of the domain walls and the Nd moment. Further investigations, e.g. magnetostriction measurements, are needed to clarify this problem.

4. Conclusion

We have studied the effects of a high magnetic field on crystals of $R_{1/2}\mathrm{Sr}_{3/2}\mathrm{MnO}_4$ ($R = \mathrm{La}$ and Nd) by means of measurements of the magnetisation and magnetoresistance up to 40 T. The $\mathrm{La}_{1/2}\mathrm{Sr}_{3/2}\mathrm{MnO}_4$ showed metamagnetic-

like transitions accompanied by colossal magnetoresistance effects which can be ascribed to the field-induced collapse of the charge ordering. These transitions become first order at low temperatures. For $Nd_{1/2}Sr_{3/2}MnO_4$, the magnetic field enhances the two-dimensionality of the conduction and induces magnetic transitions accompanied by colossal magnetoresistance effects at low temperatures.

Acknowledgments

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