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Magnetic and electrical properties of $Nd_{0.66}(Sr_{1-y}Li_y)_{0.34}MnO_3$ manganites

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Abstract

We present X-ray diffraction, magnetization, electrical resistivity, and magnetoresistance data for $Nd_{0.66}(Sr_{1-y}Li_y)_{0.34}MnO_3$ ceramics with $y=0$, 0.05, 0.1, 0.2 and 0.3 in the temperature range $50<T<400$ K and in fields up to 0.5 T. We find that Li substitution is possible up to $y\leq 0.3$ and generally enhances the resistivity and the magnetic randomization. Nevertheless, the resistivity curves still show the characteristic hump-like structure indicative of a combined ferromagnetic–paramagnetic metal–insulator transition, and a significant magnetoresistance is observed. The increase of the resistivity with Li content is ascribed to a blocking of Zener bonds associated with the charge unbalancing effect of Li^+. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The metal–insulator and magnetic transitions in GMR systems $R_{1-x}A_xMnO_3$ result from a complicated coupling between spin, charge and lattice degrees of freedom [1–5]. This is manifested, in particular, in the discovery of new ordering phenomena such as charge and orbital ordering, but also suggests that lattice excitations such as polarons and/or spin polarons are involved. The motivation for this work was to study the changes introduced by one of the factors which might modify the ground state and/or the excitations profoundly, i.e. R (rare earth) or A (alkaline earth) substitutional doping; here, however, alkaline, i.e. Li, doping. $Nd_{0.66}(Sr_{1-y}Li_y)_{0.34}MnO_3$ compounds thus belong to the wider class of GMR systems. So far, not much work has been done on alkaline earth substitution by alkali elements. Formally, when we substitute Sr^{2+} with Li^+, one would expect to increase the Mn^{3+}/Mn^{4+} disproportion towards Mn^{4+}. However, as Li^+ is considered to be a small ion, its comprehensive role is still undecided, i.e. whether it is positioned as an interstitial, occupies a Sr site, decorates existing defects or is lattice mobile as in superionic conductors. Thus another aspect enters, i.e. a possible stabilization of the properties of the (distorted) perovskite lattice via interstitial site occupation: irreversible magnetic and magnetostrictive effects are often observed in connection with the increasing spin and structural disorder. In particular, the manganites are very sensitive to oxygen or other point or line defect disorder [2,5]. Thus, we first present results for Li-doped $Nd_{0.66}Sr_{0.34}MnO_{3-\delta}$ in this contribution.

2. Experimental

Polycrystalline samples of the nominal composition were synthesized using standard ceramic techniques [6,7]. Stoichiometric proportions of Nd_2O_3, Li_2CO_3, Mn_2O_3 and $SrCO_3$ were mixed to fulfil the formal composition $Nd_{1-x}(Sr_{1-y}Li_y)_xMnO_3$, reacted in air first at 1000°C and then at 1200°C for 2 days with intermediate grindings. Using pellets of the starting powders and a slow temperature increase, Li losses were generally less then 10% of the weighed in amount. This is supported by the observed systematic behavior of the physical properties. Nevertheless, some samples were checked for loss of Li by wet chemical analysis. Powder X-ray diffraction patterns revealed an orthorhombically distorted perovskite structure

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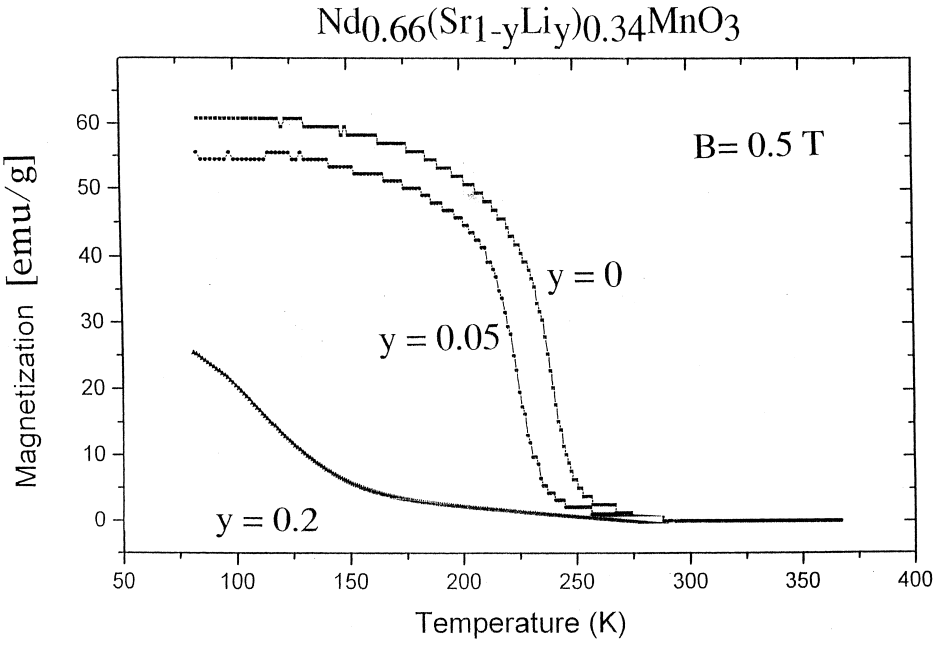
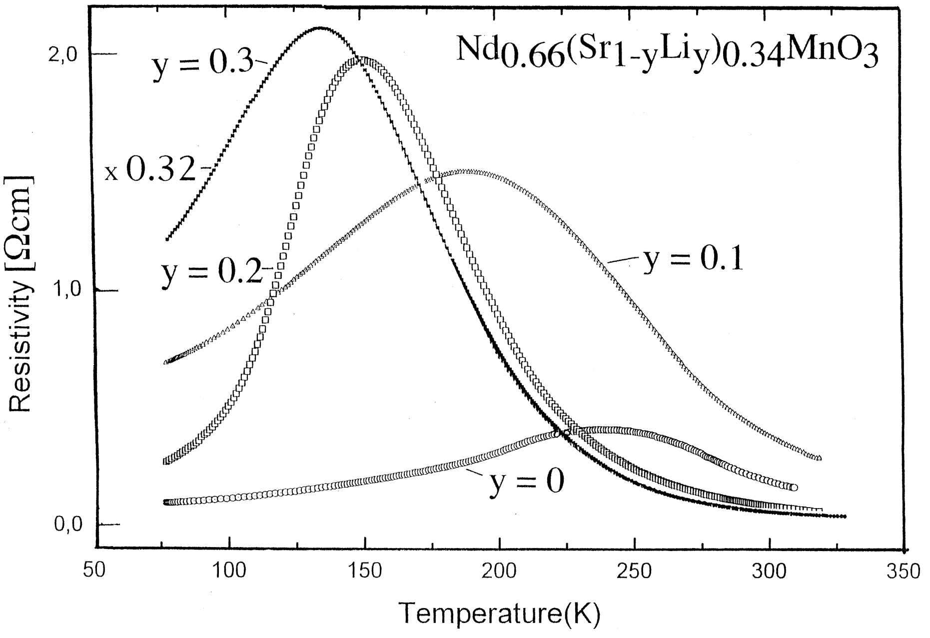
with $a = 5.4494(1)$ Å, $b = 7.6964(1)$ Å and $c = 5.4547(1)$ Å ($y = 0$), with small amounts of Mn_2O_3 (<5%). Further secondary phases were found for the compounds containing Li: $LiMnO_3$ and Li_2O_2 (<5%; $y = 0.1$). The oxygen content is also accurate to this degree. The change in the lattice parameters with increasing y up to 0.3 was less than 0.5%. As Li^+ is smaller than Sr^{2+}, this suggests that the perovskite lattice is mainly supported by the transition metal/oxygen octahedra.

For the transport measurements, the final ceramic powders were again pressed into pellets and cut into rectangular shapes to allow for the application of the four-point resistivity method. The magnetoresistance was measured using a slow pulse method, i.e. the magnet was moved mechanically on and off the cryostat while the resistivity versus temperature curve $\rho(T)$ was recorded. The Faraday method was used to obtain the magnetic moment versus temperature.



(a)



(b)

Fig. 1. Magnetization M (a) and resistivity ρ (b) for $Nd_{0.66}(Sr_{1-y}Li_y)_{0.34}MnO_3$ compounds versus temperature; $y = 0$, 0.05, 0.1, 0.2 and 0.3; the resistivity curve for $y = 0.3$ is reduced by a factor of 0.32.

3. Results and discussion

3.1. Correlation of resistivity and magnetization

Fig. 1a shows magnetization versus temperature curves $M(T)$ and Figs. 1b and 2 the resistivity curves $\rho(T)$. These data and also the concentration limit of Li are in general accord with the values found for $La_{1-x}Li_xMnO_3$ [4]. Note, in particular, the correlation between the metallic and ferromagnetic states, which is typical for double exchange systems. The peak of $\rho(T)$, which is usually ascribed to a metal–insulator transition at T_m, coincides here with the magnetic ordering temperature (Curie point, T_C), at least for small y; the peak is rather rounded off even at $y=0$, probably due to defects or an oxygen deficit in the ceramic samples.

Nevertheless, for a Li content of $y=0.05$, the peak (and T_C) are shifted to lower temperatures without any significant change in the sharpness of the structure (Fig. 1a,b). The magnetization is reduced with increasing Li content while the resistivity increases. This behavior is very similar to that found in fixed valence substituted $La_{1-x}Ca_x Mn(Fe/Ge)O_3$ and there it was ascribed to the reduction in the number of active Zener Mn^{3+}–Mn^{4+} bonds through the interference of the fixed valence sites Fe^{3+} or Ge^{4+} [3]. Assuming that the substituting portion of the Li^+ ions shifts the disproportion towards Mn^{4+}, we may either assume an increase in hole doping or an increase of blocking bonds as in the case of Ge^{4+} fixed valence substitution, i.e. $Nd_{1-x}(Sr_{1-y}Li_y)_xMnO_3$ might become more conducting with increasing y or behave similar to $La_{1-x}Ca_xMn_{1-y}Ge_yO_3$. As the resistivity increases with y, we have to reject the first possibility. With the second approach, if one Li^+ ion has the equivalent effect as one Ge^{4+} ion, then T_C would be proportional to the number of still intact valence mixed (Zener) Mn^{3+}–Mn^{4+} bonds. For $x=0.3$, small y and Mn^{3+} and Mn^{4+} in their respective octahedral settings it has been proposed that $T_C/T_o = 1 - 9.167y$ [3]. With Li doping, however, we find $T_C/T_o = 1 - (2\pm0.2)y$ (Fig. 3), suggesting that each Li^+ ion on average reduces the coupling by an average of two bonds while blocking a former Mn^{3+}–Mn^{4+} conducting path, i.e.

$$T_C/T_o = x(1-2y)/x = 1 - 2y \tag{1}$$

According to Eq. (1), at $y=1/2$, $T_C=0$ and no Zener

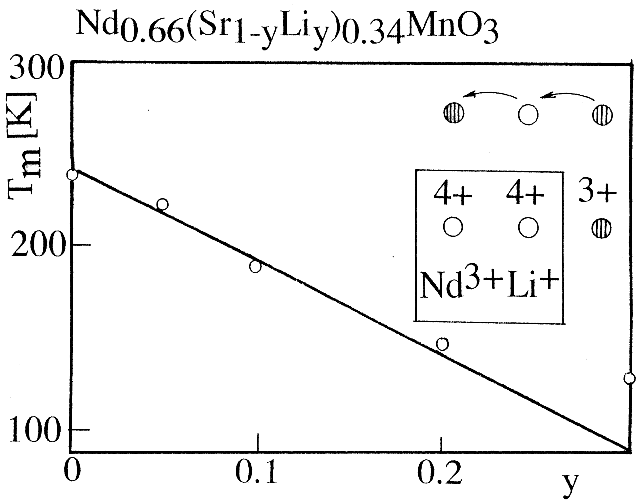


Fig. 3. Temperature of the resistivity maximum versus Li content $T_m(y)$. (———) Bond blocking model (see inset): on a $\cdots Mn^{3+}$–Mn^{4+}–Mn^{3+}–$Mn^{4+}\cdots$ percolative Zener chain, if one Mn^{3+} is changed to Mn^{4+} because of local charge conservation (one Sr^{+2} is substituted by one Li^+), the Zener chain is blocked, which increases the resistivity and decreases the ferromagnetic coupling by two bonds per one Li^+ ion.

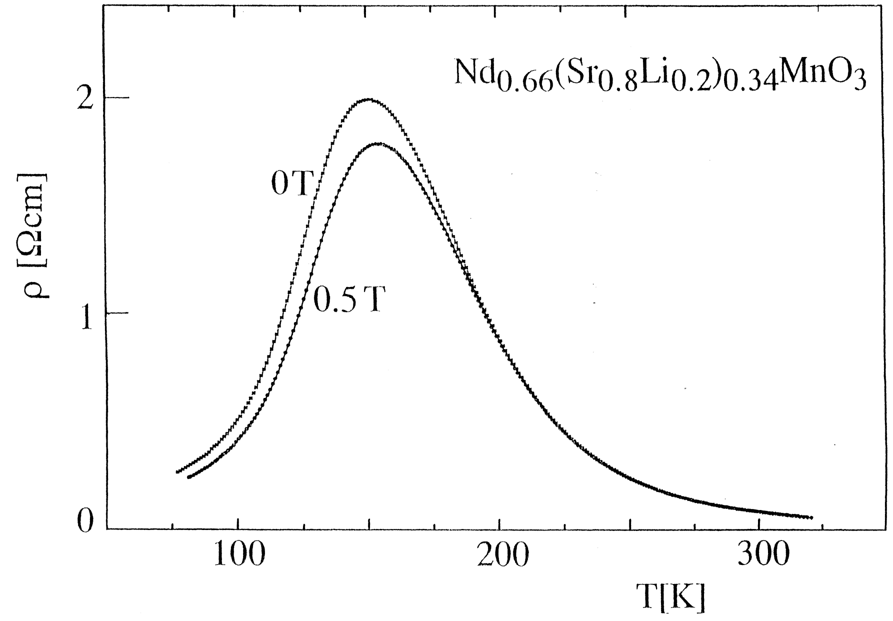


Fig. 2. $\rho(T)$ for $y=0.2$ at $B=0$ and 0.5 T.

bonds remain. Thus, we expect that, ultimately, $y = 0.5$ limits the region of existence of the Sr/Li mixed phase. Experimentally, the limit appears to be lower, at $y = 0.3$. Also, consistently, with the increase of Mn^{4+} blocking sites, we observe a reduction of M (see Fig. 1a). This we ascribe to an increase of the spin frustration associated with the increase of the competing negative Mn^{4+}–O–Mn^{4+} superexchange interactions, together with increasing randomization in both cases.

3.2. Magnetoresistance

With the manganites the volume magnetoresistance is usually largest around the metal–insulator (T_m) and ferromagnetic order–disorder transition temperature (T_C) and tends to disappear in well developed semiconducting and metallic states [4,5]. However, as metallic multilayer systems can also have magnetoresistive effects of the observed magnitude, with polycrystals the internal surfaces might provide another source of $\Delta\rho/\rho$. A rather well defined maximum of $\Delta\rho/\rho$ was found for $y = 0$ close to T_C in Ref. [6], but is superimposed on a continuous increase at low temperatures (Fig. 4). The peak is usually associated with the field-induced shift of T_m [5,6], here $dT_m/dB = 5.6$ K/T. For our $y = 0$ ($y = 0.1$) sample, one finds only a monotonous rise, although $dT_m/dB = 3.6$ K/T (7 K/T) is of the same order of magnitude. Obviously, here the magnetoresistive effects associated with spin-dependent scattering or spin-polarized tunneling on or over internal interfaces (grain boundaries, phase domains, magnetic domains, etc.) dominate. With the Li-doped samples, a maximum MR of about 20% is found for $y = 0.2$ (Figs. 2 and 4) and $dT_m/dB = 7$ K/T (Fig. 2), while for $y = 0.3$ (7.5 K/T) only a shoulder appears. With internal surface MR effects the empirical relation

$$\Delta\rho/\rho = A + B/(T + T_o) \qquad (2)$$

has been found [8], consistent with our results (A, B and T_o are empirical constants). The stability of the magnetoresistive signals is rather good, however there is as yet no proof that Li doping has a stabilizing effect.

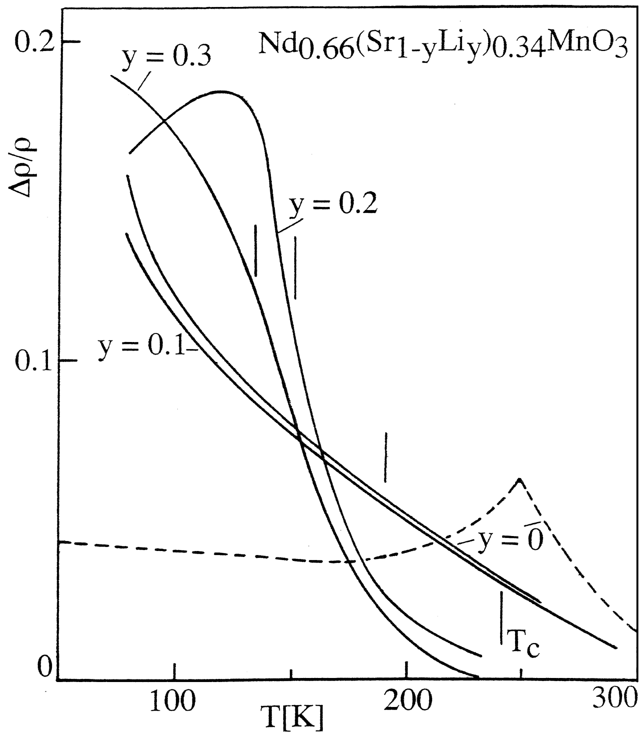


Fig. 4. Magnetoresistance $\Delta\rho/\rho$ versus temperature for $y = 0$, 0.1, 0.2 and 0.3 at 0.5 T. (- - -) Magnetoresistance according to Ref. [6] at 5 T, reduced to 0.5 T. Vertical bars indicate the T_C values observed for the four samples.

4. Conclusions

The reduction of T_C and M of $Nd_{1-x}Sr_xMnO_3$ under Li doping is correlated with Li on substitutional sites, blocking the Zener carrier paths. The observed magnetoresistance is thought to be due to a superposition of volume and internal surface effects.

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