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Thermopower and anomalous heat transport in $La_{0.85}Sr_{0.15}MnO_3$

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The thermopower and thermal conductivity of $La_{0.85}Sr_{0.15}MnO_3$ have been studied as a function of temperature and magnetic field. Huge changes of the thermopower of about one order of magnitude have been observed in the vicinity of the metal-insulator (M-I) transition. The measured relative change of the thermopower was found to be proportional to that of the resistivity. Furthermore, a magnetic-field-dependent anomaly of the thermal conductivity was found in the vicinity of the M-I transition that cannot be explained by a variation of the electric conductivity alone but requires a magnetic-field-dependent lattice contribution. This signals the importance of the lattice dynamics for understanding the details of the M-I transition. [S0163-1829(98)50310-4]

In the last years there has been renewed interest in the manganese oxides $R_{1-x}A_xMnO_3$ (R=La, Pr, Nd; A=Sr, Ca, Ba, Pb) because of their very large decrease in resistivity on applying a magnetic field. This effect is denoted as ''colossal magnetoresistance'' (CMR).[1–4] The detailed mechanism that is responsible for the CMR is not well understood so far. In particular, the question whether the ''double exchange'' mechanism proposed by Zener[5] in 1951 is sufficient for a complete description of the phenomenon or whether lattice effects have to be included, is discussed intensively.[6–8] In order to clarify the impact of lattice effects and the role of electron-lattice coupling in this paper we present measurement of thermoelectric effects and thermal transport properties of $La_{0.85}Sr_{0.15}MnO_3$. The study of these quantities is interesting since the measurement of the thermal conductivity allows us to study changes in the phononic modes as a function of temperature and magnetic field. Furthermore, the thermopower provides insight into changes of the band structure near the M-I transition.

The samples used in our study are high-quality single crystals prepared by a floating zone method. Details of the preparation technique as well as the structural, magnetic, and electrical transport properties of the samples have been published previously.[9] For the electrical characterization we used a conventional four-probe method. The thermopower and thermal conductivity were obtained by using a pulsed power technique at stabilized temperature in order to separate the sample signal from disturbing thermovoltages. In all measurements the direction of the applied electric or heat current was perpendicular to the applied magnetic field B_{ext}.

Figure 1 shows the temperature dependence of the resistivity ρ at different B_{ext}. Clearly, ρ is suppressed by about one order of magnitude for $B_{ext}=6\,\mathrm{T}$ at temperatures slightly below the ferromagnetic ordering temperature $T_c \simeq 240$ K. We note that ρ was found to be completely independent of the angle between the magnetic-field direction and the direction of the applied current. In Fig. 2 the thermopower S of $La_{0.85}Sr_{0.15}MnO_3$ is plotted as a function of temperature for different values of B_{ext}. Below about 200 K the curves measured at different fields are almost indistinguishable, that is, almost no magnetic-field dependence is observed in this regime. Figure 2(b) shows the data of Fig. 2(a) around the M-I transition on an enlarged scale. Comparison of the data of Fig. 1 and 2(b) clearly shows that the T and B_{ext} dependence of S and ρ are qualitatively the same. To further illustrate this observation, in Fig. 3 we show $S(T)$ and $\rho(T)$ for $B_{ext}=0$ and 2 T, respectively. In order to establish a quantitative relation between S and ρ, in Fig. 4 the relative change $\Delta S/S_0=[S(T)T_0/T-S(T_0)]/S(T_0)$ of the thermopower is plotted versus the relative change $\Delta\rho/\rho_0=[\rho(T)-\rho(T_0)]/\rho(T_0)$ of the resistivity for $T_0=200$ K. The experimental data clearly show a proportionality between these relative changes. A possible explanation for this behavior has been given recently by Asamitsu *et al.*[10] based on Mott's formula

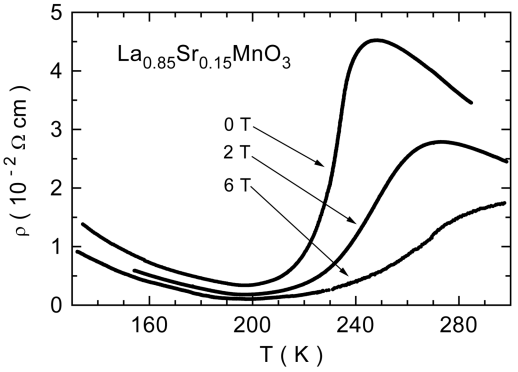

FIG. 1. Resistivity versus temperature of $La_{0.85}Sr_{0.15}MnO_3$ at different magnetic fields.

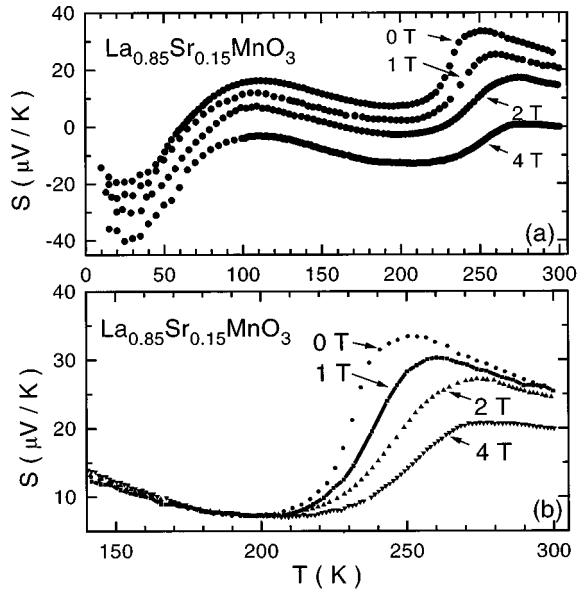

FIG. 2. Thermopower S of $La_{0.85}Sr_{0.15}MnO_3$ versus temperature for different applied magnetic fields. For clarity, in (a) the curves are shifted downwards by 5 μV/K per T. In (b) the temperature regime around T_c is shown on an enlarged scale.

$$S = -\frac{\pi^2}{3}\frac{k_B^2 T}{e}\frac{\sigma'(E_F)}{\sigma(E_F)}, \tag{1}$$

where k_B is Boltzmann's constant, e the elementary charge, $\sigma(E_F)$ the conductivity at the Fermi level and $\sigma' = (\partial/\partial E)\sigma(E)$. For metals, $\sigma(E_F)$ is equal to the electrical conductivity σ.[12] In the discussion given by Asamitsu *et al.*[10] it was assumed that $\sigma' \approx$ const. However, this assumption may not be valid for our moderately doped sample in the vicinity of the M-I transition. It is well known that σ' includes the effective mass of the charge carriers and, hence, the band structure. According to our experience, the band structure, and in turn σ', changes on passing the M-I transition. To further clarify this point we return to Fig. 4. According to Mott's formula, $\Delta S/S_0 \propto \Delta\rho/\rho_0$ is expected (dashed lines in Fig. 4), if one assumes $\sigma' =$ const and almost

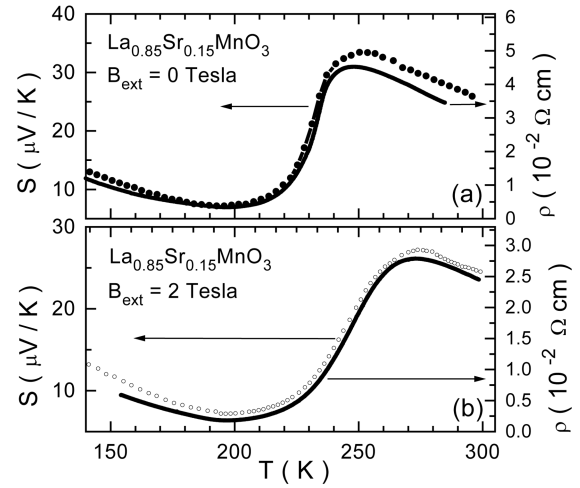

FIG. 3. Thermopower and resistivity of $La_{0.85}Sr_{0.15}MnO_3$ plotted versus temperature for $B_{ext} = 0$ T (a) and $B_{ext} = 2$ T (b).

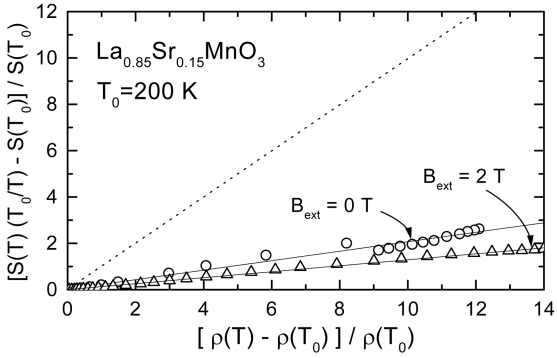

FIG. 4. Relative changes of the thermopower plotted versus relative changes of the resistivity for $La_{0.85}Sr_{0.15}MnO_3$ at $B_{ext} = 0$ and 2 T. The dashed line represents the prediction of Mott's formula.

isotropic electrical transport properties, i.e., $\sigma^{-1} = \rho$. Evidently, our data deviate from this theoretical prediction by a factor of about 3–5 suggesting that the assumption $\sigma' \approx$ const is indeed not justified. We also note that S changes sign at about 61 K. This sign change and the complicated T dependence of S in the low-T regime are similar to that observed in doped La_2CuO_4 and most likely are related to charge ordering phenomena.[11]

We also measured ρ and S as a function of B_{ext} at fixed temperature. The result for $T = 239$ K, i.e., just below T_c, is shown in Fig. 5. Both quantities show a strong monotonous decrease with increasing applied field. In analogy to the term ''colossal magnetoresistance,'' we denote the very large suppression of S by B_{ext} as ''colossal magnetothermopower'' (CMT).

There is an obvious qualitative explanation for the observed behavior of S. It is well known that bad conductors have, as a rule of thumb, a larger S than good conductors and vice versa. Hence, near a M-I transition, S is expected to vary in the same way as ρ. The main parameter for the change of ρ and S is, at least within the scope of the double exchange model, the magnetization M that depends both on T and B_{ext}. Hence one expects

$$S = f_1(M(T, B_{ext})),$$

$$\rho = f_2(M(T, B_{ext})), \tag{2}$$

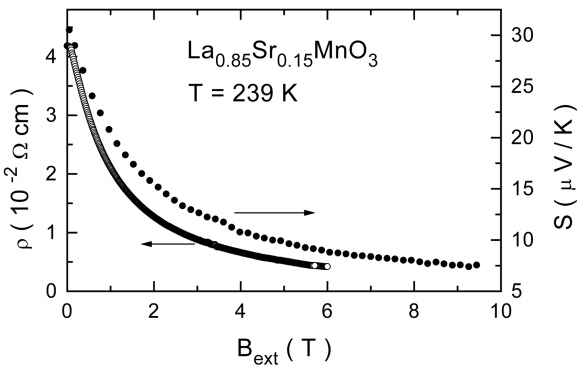

FIG. 5. Resistivity and thermopower of $La_{0.85}Sr_{0.15}MnO_3$ at $T = 239$ K as a function of applied magnetic field B_{ext}.

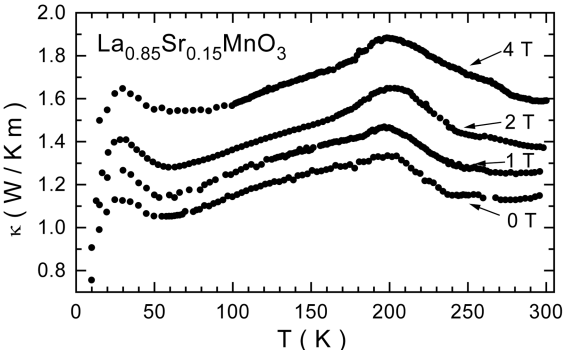

FIG. 6. Total thermal conductivity κ as a function of temperature at different applied magnetic fields. The curves are shifted upwards by 0.1 W/K m per T for clarity.

where f_1 and f_2 should be ''monotonous'' functions, i.e., they should not show any kinks, jumps, oscillations, or divergencies. From these equations it can be easily derived that $S=f_1(f_2^{-1}(\rho))$, where $f_1(f_2^{-1}(\rho))$ should be ''monotonous,'' too. This is well confirmed by our experimental data. Further conclusions or even a quantitative evaluation of our data are not possible at present.

Next we discuss the thermal conductivity κ of $La_{0.85}Sr_{0.15}MnO_3$. In Fig. 6, $\kappa(T)$ is plotted for different B_{ext}. The first thing to note is the small value of κ, of the order of only 1 W/K m, typical of amorphous materials.[13] Comparable values have been reported recently by Visser *et al.*[14] for Pb, Ca, and Nd-doped $LaMnO_3$. The second thing to be discussed is the low-temperature behavior ($T<50$ K). Clearly, there is a local maximum in $\kappa(T)$ at around 25 K. Since $\rho(T)$ increases exponentially upon lowering T, $La_{0.85}Sr_{0.15}MnO_3$ can be considered as an insulator at low T. It is well established that most insulators show a local maximum in $\kappa(T)$ at low T as observed in our experiment, since κ first should increase as T^3 and then decrease as $e^{\Theta_D/2T}$ upon increasing T. Here, Θ_D is the Debye temperature. The third interesting feature is the positive slope $d\kappa/dT$ over the intermediate T regime from about 50 to 200 K. We note that this T range of positive $d\kappa/dT$ is well below T_c. This is in contrast to recent experiments by Visser *et al.*[14] who found $d\kappa/dT>0$ for $T>T_c$ and attributed this observation to anharmonic lattice distortions. In order to discuss possible origins of the positive $d\kappa/dT$ in our sample we note that the thermal conductivity and the specific heat have a similar temperature dependence in this regime. Based on a kinetic expression for the thermal conductivity, $\kappa=nCvl$, where n is the density of entities transporting heat, C the specific heat, v the group velocity, and l the mean free path, this suggests that l is almost independent of T. Whether this is caused by a strong disorder of the bond lengths[15] or by charge ordering phenomena and what actually are the entities contributing to the heat transport have to be clarified by future experiments.

In the following we focus on the T regime around the M-I transition. In our discussion we assume that the measured total thermal conductivity κ consists of mainly two dominating parts, namely an electronic contribution κ_{el} and a phononic contribution κ_{ph}, i.e., $\kappa=\kappa_{ph}+\kappa_{el}$. The basic question that has to be addressed is whether the M-I transition changes only κ_{el} or both κ_{ph} and κ_{el}. In this context we

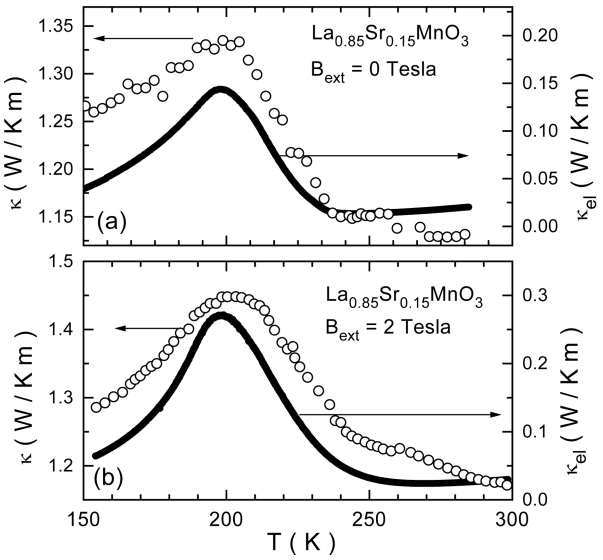

FIG. 7. Comparison of the temperature dependence of the electronic and the total thermal conductivity of $La_{0.85}Sr_{0.15}MnO_3$ at $B_{ext}=0$ T (a) and $B_{ext}=2$ T (b).

note that an estimate of κ_{el} can be obtained from the Wiedemann-Franz law $\kappa_{el}/\sigma=LT$, where σ is the electrical conductivity and $L=2.45\times10^{-8}$ W Ω/K^2 the Lorenz number. As shown in Fig. 6, κ increases considerably below T_c. This is just the same temperature regime where also σ increases suggesting that the increase in κ may be caused simply by an increase of κ_{el}. To clarify this issue, in Fig. 7 we have plotted κ_{el} derived from the measured resistivity data by using the Wiedemann-Franz law together with the measured κ. It is evident that the measured κ value is substantially larger than the derived value of κ_{el}. This clearly shows that the major part of κ has to be attributed to lattice vibrations. On the other hand, the maximum in $\kappa(T)$ can be well explained in terms of an increased electrical conductivity. In order to further separate the phononic and electronic contributions to κ, in Fig. 8(a) we have plotted the difference $\kappa(2\text{ T})-\kappa(0\text{ T})$ for $B_{ext}=2$ T. Assuming that κ_{ph} is independent of B_{ext}, one expects $\kappa(2\text{ T})-\kappa(0\text{ T})\simeq LT[\sigma(2\text{ T})-\sigma(0\text{ T})]$. This is clearly satisfied for $T\leqslant200$ K. That is, our data give strong evidence that κ_{ph} is completely independent of B_{ext} far below T_c. On the other hand, above 200 K there seems to be a clear magnetic-field dependence of κ_{ph}. However, it still has to be discussed whether this effect can be explained in terms of a T-dependent Lorenz number in the Wiedemann-Franz law. In order to clarify this point we consider the absolute value of $\kappa_{el}(2\text{ T})-\kappa_{el}(0\text{ T})$ between 230 and 250 K, which amounts to about 0.025 W/K m. The corresponding value of $\kappa(2\text{ T})-\kappa(0\text{ T})$ is larger by a factor of 2–3. In order to explain this discrepancy by electronic changes alone, the Lorenz number has to change by a factor of 2 or 3. Furthermore, this means that the electrons must transport heat much better than electrons in a metal. There is no obvious argument for such a behavior. The most striking argument against an explanation in terms of the Wiedemann-Franz relationship comes from the fact that the peaks in the $\kappa_{el}(2\text{ T})-\kappa_{el}(0\text{ T})$ and the $\kappa(2\text{ T})-\kappa(0\text{ T})$ curve occur at different temperatures [see Fig. 8(a)]. This clearly illustrates

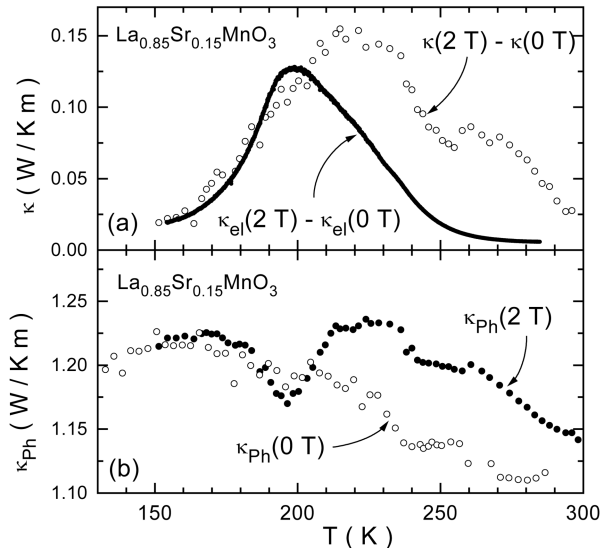

FIG. 8. (a) difference between total and electronic thermal conductivities at $B_{ext}=0$ and 2 T plotted versus temperature. In (b) the phononic thermal conductivity $\kappa_{ph}=\kappa-\kappa_{el}$ is shown as a function of temperature for $B_{ext}=0$ and 2 T.

that the respective scattering processes are related indirectly via electron-lattice coupling and not directly via the Wiedemann-Franz law.

There is a simple qualitative explanation for the magnetic-field-dependent κ_{ph}. At low temperatures, the magnetization M of the sample is completely saturated. However, this is no longer true for higher temperatures. Furthermore, it is known from the measurement of thermal expansion,[16] that the lattice constants change considerably near T_c. For example, the lattice constants of $La_{7/8}Sr_{1/8}MnO_3$ in the ferromagnetic phase have been found to differ by more than 1% from those in the paramagnetic phase. This means that the lattice constants depend on the order parameter M. The magnetic phase transition is obviously coupled to a spontaneous lattice distortion. In this situation it is likely that fluctuations of the order parameter M are related to fluctuations of the lattice constants. These fluctuations in turn result in an additional phonon scattering. In the presence of a strong external magnetic field the fluctuations are partly suppressed and the additional scattering channel is strongly suppressed. Accordingly, the phononic thermal conductivity is expected to increase around T_c when applying a magnetic field. At low temperatures, M is almost saturated and the contribution of B_{ext} to the magnetic moment is small. Therefore, in this temperature regime no field dependence of κ_{ph} is expected. This behavior agrees well with the data shown in Fig. 8. We note that a linear increase of κ is obtained at fixed temperature upon increasing B_{ext}. At $T=200$ K this increase amounts to about 5%/T.

In summary, we have found a proportionality between the thermopower and resistivity in moderately Sr-doped $LaMnO_3$ close to the M-I transition. A qualitative explanation of this behavior and a critical discussion of a modeling in terms of Mott's formula are given. In the vicinity of the M-I transition the thermal conductivity shows a magnetic-field-dependent anomaly that can be explained only in part by an increased electrical conductivity and the Wiedemann-Franz law. For a complete explanation of the anomaly a magnetic-field-dependent phononic contribution to the thermal conductivity is required. This signals the importance of the lattice dynamics and implies that the CMR transition may not have a purely electronic origin.

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