



Magnetic field dependent thermal conductance in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$



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ABSTRACT

Using the differential 3ω technique we measured the low-temperature out-of-plane thermal conductance of heteroepitaxial thin film $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO). The magnetic field dependence of the thermal conductance reached values of up to 23%. The effect was observed to be largest in the vicinity of the metal–insulator transition, since the enhancement in thermal conductance is triggered by the colossal magnetoresistance effect increasing the electronic contribution to the thermal conductance. The point of the maximal change was adjusted by post-annealing the samples in an oxygen atmosphere. Samples with a higher transition temperature and lower epitaxial strain displayed a lower magnetic field dependence of up to 8% of the zero-field value. While the samples with a low strain state seemingly obeyed the Wiedemann–Franz law, those under high strain did not. Raman spectroscopy was applied to explain this discrepancy by an enhanced phononic density of states caused by rotational distortions of the unit cell. Our results show that in systems with strong electron–lattice interaction manipulation of the phonon spectrum is possible by magnetic fields.

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1. Introduction

In the 1950s, the calcium doped lanthanum manganites $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ have drawn considerable attention due to their colossal magnetoresistive properties (CMR, Refs. [1,2]) accompanied by a transition from a ferromagnetic to a paramagnetic state. The physical origin of these effects was unclear until the late 1990s, when new experimental insights allowed a deeper understanding of the phenomena within the material class such as an explanation of the transport properties in a setting of strong electron–lattice coupling and the complex phase diagram in terms of doping [3,4]. In the case of $x=0.33$ the compound (hereafter denoted as LCMO) displays a metal–insulator transition at $T_{MI} = 230$ K and a ferromagnetic-to-paramagnetic phase transition at a slightly higher temperature (for a thorough review of the transport properties see Ref. [5]). The reason for these almost coinciding phase transitions lies within the temperature dependent exchange interactions between the Mn atom in the center of the unit cell, the oxygen octahedron surrounding it, and the neighboring Mn atoms. The interaction causes a dynamic interplay between the spin state of the Mn atom and the Jahn–Teller-lifted degeneracy of the conduction band (for reviews see e.g. Refs. [2,6]). Finally, epitaxial strain can lead to changes in the transition

temperature and in the magnitude of the CMR [7].

While the magnetoresistive transport mechanism is well understood, the magnetocaloric implications are not extensively studied in single crystalline thin films. Visser et al. [8] solely studied polycrystalline manganites. The CMR effect is commonly expressed as a magnetoresistive value and can be defined as $\text{CMR} = (R_{B=0} - R_{B \neq 0})/R_{B \neq 0}$. This definition yields positive values that can be larger than 100%. The CMR effect should contribute to the thermal conductance.¹ This effect is in the following termed magnetothermal resistance (MTR) and is defined in analogy to the CMR as the ratio between thermal conductances κ to

$$\text{MTR} = \frac{1/\kappa_{B=0} - 1/\kappa_{B \neq 0}}{1/\kappa_{B \neq 0}} = \frac{\kappa_{B \neq 0} - \kappa_{B=0}}{\kappa_{B=0}}. \quad (1)$$

The heat conductivity is usually decomposed in a phononic and an electronic contribution as $\kappa = \kappa_{ph} + \kappa_e$. For the latter in simple metals the Wiedemann–Franz law is valid, i.e. the electronic thermal conductivity is in this case expected to relate to the electrical conductivity σ , the specific resistivity ρ and the temperature T as

¹ Strictly speaking, the quantity measured here is thermal conductance. Thermal conductivity is a bulk property, as the characteristic length scale of the heat conduction equation is not necessarily smaller than the thickness of the thin film, which leads to a thickness dependence.

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$$\frac{\kappa}{\sigma} = \kappa_e \rho = L_0 T. \quad (2)$$

Here, the Lorenz number L_0 is assumed to be constant with temperature as originally expected from Drude theory. In order for the Wiedemann–Franz relation to be valid the electron scattering processes that degrade the electrical conductivity need to be predominantly elastic, which is an assumption not necessarily fulfilled for materials with strong electron phonon coupling as doped perovskites. Additionally the mechanism of conductivity changes at the metal–insulator transition from metallic at low temperatures to thermally activated at high temperatures [9], such that the applicability of the Wiedemann–Franz relation is questionable. In addition, the Wiedemann–Franz relation is not fulfilled in the vicinity of the Debye temperature, which lies at approx. 400 K [10]. Nevertheless it provides the most commonly used relation between electronic thermal and electrical conductance. Therefore we chose this relation for our discussion in spite of its deficiencies, as it distinctly demonstrates deviations from free-electron behavior. While the decrease of the electrical resistivity (the CMR) can be of the order of several hundred percent in the case of phase transitions taking place in the low-temperature regime [4], the size of MTR is limited by the phononic contribution to the thermal conductance. As the latter can by far exceed the electronic part [6] an effect on the thermal conductance caused by the CMR is potentially difficult to measure. Despite this, strong electron–phonon coupling can influence the electronic contribution and therefore increase the MTR above the Wiedemann–Franz expectation [8].

Raman scattering is a valuable tool that is sensitive to phononic degrees of freedom and thus provides complementary information to our transport measurements. Raman spectra of manganites generally consist of sharp features with energies according to selection rules of first order Raman scattering in a defined scattering geometry and broad features corresponding to higher order phononic and electronic processes [11]. One of the earliest discussions of the importance of Raman scattering in the understanding of the many-fold interactions between subsystems of LCMO was presented by Podobedov et al. [11], who studied epitaxial LCMO grown by pulsed laser deposition on LaAlO₃ (LAO) and NdGaO₃ (NGO) substrates and found no difference between the spectra. Abrashev [12] extended this research towards SrTiO₃ (STO), yttria stabilized zirconia (YSZ) and MgO substrates. Abrashev [13] considered Jahn–Teller bands in perovskite-like manganites in general. They subdivided Jahn–Teller distortions into those caused by small structural perturbations and those caused by structural transitions and large incoherent Jahn–Teller distortions. The latter can break the translation symmetry along given directions and phonons normally not Raman active can be visible. Thus these features in the Raman spectra are rather related to the phononic density of states (DOS) than to specific Raman modes. A more detailed study was carried out by Pantoja et al. [14], who presented mode assignments based on the symmetries of the $Pnma$ space group and confirmed the interpretation of specific Raman modes as such phononic contributions. Abrashev et al. [15] proceeded to perform lattice-dynamical calculations according to Popov [16] on the parent compound CaMnO₃ (CMO). The resulting Raman intensities of active modes in CMO are then transformed into those of distorted structures as observed in LCMO. Using what they termed ‘basic distortions’, the authors calculated the expected frequencies of the corresponding modes and correlated them to the measured spectra. The result indicated that the suggestion of Podobedov et al. [11], attributing certain modes to purely phononic densities of state, was indeed valid.

2. Experimental

A series of LCMO samples with different thicknesses (25 nm, 100 nm, 200 nm and 400 nm) were grown heteroepitaxially on STO, MgO and LAO substrates in (100) orientation by KrF pulsed laser deposition at a pulse rate of 5 Hz with an energy density of 1.2 J/cm². Optimal growth conditions were found at a pure oxygen pressure of approx. 10 Pa and substrate temperatures between 650 °C and 850 °C. Some samples were post-annealed in an oxygen atmosphere at 950 °C for two hours to improve oxygen stoichiometry and thereby adjust the metal–insulator transition temperature by altering the bond angle between two oxygen atoms and the intermediate manganese atom. As a consequence, the magnetic phase transition temperature and the metal–insulator transition temperature are increased [17]. The thermal conductance finally is measured by means of the 3ω method, which requires a stack of 200 nm of Al₂O₃ and 50 nm of Au to be sputtered on top of the LCMO thin film. The Au capping layer was structured by UV lithography into a bar with $b = 20 \mu\text{m}$ width and a length of $l = 1 \text{ mm}$.

The thermal conductance is measured by the 3ω method [18,19], in which a patterned structure is used as a heater and a measurement device for the thermal resistivity of the sample simultaneously. An alternating current with frequency ω is applied to the heater structure, heating the sample with a frequency of 2ω . This heating causes the resistance of the heater itself to oscillate periodically with the same frequency. Inserting this into Ohm’s law and simplifying the expression using trigonometric identities result in an expression for the measurement voltage with a 1ω and a 3ω contribution:

$$U = R_0 I_0 \cos(\omega t) + \frac{I_0 \Delta R(\Delta T)}{2} [\cos(3\omega t + \phi) + \cos(\omega t + \phi)]. \quad (3)$$

Here, ΔT is the temperature oscillation within the sample. Following the derivation of Cahill [19,20], the temperature oscillation in the film is related to the response voltage $U_{3\omega}$ by

$$\Delta T = \frac{2}{dR} R \frac{U_{3\omega}}{U_\omega} \quad (4)$$

and depends on the heater’s temperature coefficient of resistance $1/R \cdot dR/dT$ and on the electric heating power applied via U_ω . Finally, the size of the penetration depth of the ‘thermal wave’ compared to the sample thickness needs to be considered. At frequencies below 10 kHz the thermal penetration depth by far exceeds the film thickness, and therefore any measurement would contain a dominant substrate contribution. To avoid this, thin film thermal conductances are measured by means of a differential method, i.e. by measuring two samples with different film thicknesses. Defining ΔT_{film} as the difference between the temperature oscillations in the sample and the reference sample and calculating the area below the heater as $A = bl$ result in an expression for the thermal conductance of the additional material in the sample compared to the thin reference sample:

$$\kappa = \frac{P d_{\text{film}}}{bl \Delta T_{\text{film}}}. \quad (5)$$

Reference samples were identically grown and structured and had a film thickness of 50 nm. The use of the differential method with a reference sample eliminates the need for a separate determination of the substrate thermal conductance, the conductivity of the insulating layer and the thermal interface resistances. The thermal conductance of the samples was measured in a ⁴He cryostat at temperatures between 280 K and 60 K. A variable temperature insert (VTI) allows the sample temperature

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