

# THESES OF THE Ph.D. DISSERTATION

## Magnetic phase diagram of correlated *d*-electron systems

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# Introduction

The understanding of the properties of correlated electron systems is one of the long-standing challenges in modern solid state physics. The classical way, i.e. discussing the charge carriers in an effective one-electron picture loses its validity, the electron-electron interactions become strong and can not be treated perturbatively. This is especially true in the case of  $d$ -electron systems, where the coexistence of the different charge, spin, orbital, and lattice degrees of freedom produces a rich variety of symmetry-breaking ground states. The diversified phase diagrams mostly result from the competition of the degrees of freedom, and can be explored by utilizing the temperature, magnetic field, hydrostatic pressure as well as the chemical substitution as control parameters. Alloying elements with different ionic radii affects the lattice constant and thus the overlaps between neighboring electronic states. More importantly, it also introduces quenched disorder to the lattice leading to profound differences compared to ordered systems.

The various properties of these systems inspire both theoreticians to understand the existing phenomena and to predict new ones, as well as experimental physicists to produce new results for a more comprehensive picture by applying a wide variety of methods. These goals often imply the development of new, novel methods, sometimes resulting in even more unexpected discoveries.

## Objectives

In the framework of my Ph.D. studies I have investigated three compounds,  $\text{BaVS}_3$ ,  $\text{RE}_{0.55}\text{AE}_{0.45}\text{MnO}_3$  manganites and  $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$  ruthenates, representing different families of the strongly correlated  $d$ -electron systems. They exemplify the characteristic diversities of the  $d$ -electron systems.

### **BaVS<sub>3</sub>**

Although the onset of the metal-to-insulator transition of  $\text{BaVS}_3$  occurring at  $T_{\text{MI}} \approx 70$  K has been known for three decades, the coherent understanding of the driving force of the phase transition and of the nature of the neighboring phases is still missing. To date the experimental results are explained in terms of two co-existing  $d$ -type electronic states, the delocalized  $a_{1g}$  and the localized  $e_g$  states. The simultaneous measurement of the thermal conductivity and the specific heat provides a powerful tool to explore the interplay between these two electronic states in a more detailed manner: While the values of the thermal conductivity are affected mainly by the delocalized states, the

specific heat is more sensitive to the properties of the localized electrons. In order to exploit these properties I have developed and successfully applied a novel method for the simultaneous, high-precision measurement of the thermal conductivity and specific heat. The new experimental setup has been developed with special emphasis on elimination of the systematic errors arising from radiative heat loss, and can also be applied for single crystals with any shape.

The metal to insulator transition of  $\text{BaVS}_3$  is sensitive to pressure, but it is unclear if the low temperature magnetically ordered phase is also suppressed with hydrostatic pressure. To investigate the high-pressure behavior of  $\text{BaVS}_3$  I have studied the pressure-temperature-magnetic field phase diagram by magneto-transport measurements.

### **$\text{RE}_{0.55}\text{AE}_{0.45}\text{MnO}_3$ manganites**

In order to explore the detailed mechanism of the colossal magnetoresistance (CMR) characteristic to the  $\text{RE}_{0.55}\text{AE}_{0.45}\text{MnO}_3$  manganites I have studied an extended regime of the bandwidth-temperature-magnetic field phase diagram of the  $\text{RE}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$  family exhibiting a high level of quenched disorder. The possibility that the first-order nature of phase transitions can be preserved also in strongly disordered three-dimensional systems has received an increased attention recently. This issue can be appropriately addressed by the experimental studies of the CMR effect and orbital order-disorder transitions in manganites.

### **$\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$ ruthanates**

Due to innovations in the combinatorial methods of sample synthesis, special, composition-spread epitaxial thin films can be synthesized where the stoichiometric ratio of the components changes monotonously with the position in the sample. Studying these samples, the phase transitions and the concentration-dependent magnetic phase diagram can be mapped and characterized. I investigated the magnetic criticality of  $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$  by magneto-optical Kerr spectroscopy, a tool to measure the local magnetization of the composition-spread epitaxial thin films. For this purpose I have developed a cryogenic magneto-optical microscope which enables the resolution of local magnetic properties as a function of the Ca concentration on a  $\sim 20\mu\text{m}$  length scale. As a further improvement I adapted the method for the high-resolution, optical measurement of the ac-susceptibility by the application of a miniature Helmholtz coil.

# Methods

Due to the rich phase diagrams of the examined families of compounds, I had to apply a wide variety of methods to study the different properties of phases and phase transitions. During my work I often encountered problems which could not be solved with the conventional techniques and required the development of new methods and experimental setups. Amongst these innovations I would like to emphasize the above mentioned cryogenic magneto-optical microscope capable of measuring local magnetization and ac-susceptibility of epitaxial thin films with a vertical resolution of  $\sim 20 \mu\text{m}$ , and the novel method for the measurement of the thermal properties of samples with arbitrary shape.

Most of the experiments were carried out in the Low Temperature Physics Laboratory of the Department of Physics at the Budapest University of Technology and Economics, but I also had the opportunity to conduct measurements, as part of different scientific collaborations, in other institutes: I performed high-pressure magnetization studies as a guest of the University of Tokyo in Tsukuba, and part of the transport measurements on  $\text{BaVS}_3$  were carried out in the Department of Physics at the EPFL in Lausanne.

## New scientific results

The major conclusions of my Ph.D. work are summarized in the following thesis points:

1. I studied an extended region of the bandwidth–temperature–magnetic-field phase diagram of  $\text{RE}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$  colossal magnetoresistance manganites. The increase of the one-electron bandwidth was controlled mainly via the chemical composition of the rare earth (RE) atoms (RE=Gd, Eu, Sm, and Nd), while the fine tuning was made by hydrostatic pressure. Complementing the studies of infrared optical spectroscopy with dc resistivity and magnetization measurements I found that the enhanced phase fluctuations, namely the short-range charge and orbital correlations play a crucial role in the mechanism of the CMR effect. These fluctuations dominate the paramagnetic region of the phase diagram above all the different ground-state phases. By studying the pressure-dependence of the magnetic phase diagram I have shown that the first-order nature of the temperature-induced paramagnetic–ferromagnetic transition is robust against the quenched disorder. Towards larger bandwidth the critical temperature is remarkably enhanced, while the fluctuations become less relevant in the vicinity of the transition; thus, the first-order nature weakens. On the other hand, the CMR effect is suppressed parallel with the reduction of the resistivity change upon the transition. Finally, at a multicritical end point

the fluctuation-induced first-order transition is replaced by the usual second-order ferromagnetic transition. The colossal magnetoresistance does still exist beyond this point but it is even less effective [1, 2].

2. I studied the local magnetization of a composition-spread epitaxial thin film of  $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$  with magneto-optical Kerr spectroscopy to map and characterize the concentration-dependent magnetic phase diagram. I have found that the so called smeared region of the zero temperature concentration-dependent magnetization in the vicinity of the critical point of the clean system can be well described with a model of itinerant spin system in the presence of quenched disorder. To investigate the magnetic criticality of  $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$  I have developed a cryogenic magneto-optical microscope, which is applicable to detect the magnetic properties with a lateral resolution of  $\sim 20\ \mu\text{m}$ . The sensitivity of the microscope is  $\sim 10^{-10}$  emu, which, in the case of ultra thin magnetic films, can not be achieved by other methods. As a further improvement, by applying a miniature Helmholtz coil, I adapted the method for the high-resolution, optical measurement of the ac-susceptibility. The sensitivity of this novel technique is  $1,5 \cdot 10^{-3}$  (SI), by which the magnetic transition can be followed in the temperature sweeps of the ac-susceptibility, even in the diluted part of the sample, where the magnetization – despite the improved sensitivity – is no longer detectable with sufficient accuracy [*to be published*].
3. I have developed a novel method for the simultaneous, high-resolution measurement of the  $\kappa$  thermal conductivity and  $c$  specific heat, with special emphasis on the elimination of the systematic errors arising from radiative heat loss. The new experimental setup can be applied for single crystals with any shape over a broad range of temperature from  $\sim 3\ \text{K}$  up to  $1000\ \text{K}$ . A self-consistent data evaluation method is implemented which takes the effects of the sample geometry on  $c$  and  $\kappa$  properly into account. The new method was successfully applied to three compounds from the family of strongly correlated electron systems, namely to  $\text{BaVS}_3$ ,  $2H\text{-TaSe}_2$  and  $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$  single crystals. The differences in their thermal properties and their highly sample-dependent sizes and shapes demonstrate the extended scope of the proposed method. Additionally, one can give a rough estimation for the sample emissivity based on the results obtained by the present method [3].
4. Using the new experimental setup described in the previous thesis point, I have determined the thermal conductivity and the specific heat of a  $\text{BaVS}_3$  single crystal in the temperature regime of  $3 - 300\ \text{K}$  [3]. After the subtraction of the phonon contribution from the thermal conductivity of the high-temperature metallic phase,

I could compare the electronic and the heat transport. I found that the thermal conductivity and the electrical conductivity can be scaled together in the whole temperature regime above the metal to insulator phase transition, even in the broad precursor region above the transition, where correlations characteristic to the insulating phase are significant. The comparison resulted in an unusually high Lorentz number, signifying the enhancement of the effective mass due to charge correlations. This observation underlines the so called "bad metal" behavior of BaVS<sub>3</sub> [*to be published*].

5. By analyzing the specific heat of BaVS<sub>3</sub> I have determined the entropy variation through the subsequent phase transitions. I have shown that by decreasing the temperature from room temperature first the orbital degrees of freedom freeze out in the temperature regime ranging from the  $T_S$  structural to the  $T_{MI}$  metal to insulator transition. I found that this is followed by the freezing out of the spin degrees of freedom in the vicinity of the metal to insulator transition at  $T \sim 70$  K, which confirms the appearance of the spin gap in the nonmagnetic regime of the insulating phase. This observation supplies direct evidence for the coupling between the structural transition (driven by the delocalized  $a_{1g}$  electrons) and the magnetic correlations of the localized  $e_g$  electrons at the metal to insulator transition. The onset of the long-range, incommensurable antiferromagnetic order at  $T_X \approx 30$  K affects the low temperature behavior of the electronic entropy only to a small extent [*to be published*].
6. I studied the pressure–temperature–magnetic field phase diagram of BaVS<sub>3</sub> by magneto-transport measurements in the vicinity of the critical pressure by applying high magnetic fields comparable to the thermal energy ( $\mu_B B \sim k_B T$ ). I have shown, that the system can be driven into the metallic state at a fixed temperature solely by the application of magnetic field: The main effect is not the reduction of the transition temperature, but the broadening of the transition due to the applied field [4, 5].

## Publications related to the thesis points

- [1] Kézsmárki I., Tomioka Y., Miyasaka S., Demkó L., Okimoto Y., and Tokura Y. *Optical phase diagram of perovskite-type colossal magnetoresistance manganites with near-half doping*. Phys. Rev. B **77**, 075117 (2008).
- [2] Demkó L., Kézsmárki I., Mihály G., Takeshita N., Tomioka Y., and Tokura Y. *Multicritical end-point of the first-order ferromagnetic transition in colossal magnetoresistive manganites*. Phys. Rev. Lett. **101**, 037206 (2008).
- [3] Demkó L., Kézsmárki I., Csontos M., Bordács S., and Mihály G. *Improved thermal relaxation method for the simultaneous measurement of the specific heat and thermal conductivity*. Eur. Phys. J. B [to be published] (2009).
- [4] Fazekas P., Penc K., Radnóczy K., Barišić N., Berger H., Forró L., Mitrović S., Gauzzi A., Demkó L., Kézsmárki I., and Mihály G. *The electronic structure and the phases of  $BaVS_3$* . J. Magn. Magn. Mater. **310**, 928 (2007).
- [5] Fazekas P., Barišić N., Kézsmárki I., Demkó L., Berger H., Forró L., and Mihály G. *Magnetic-field-induced transition in  $BaVS_3$* . Phys. Rev. B **75**, 035128 (2007).