István KÉZSMÁRKI

# Phase Diagram of a Correlated *d*-electron System: Experimental Study of $BaVS_3$

**Summary of the Ph.D. thesis**

Supervisor: Prof. György MIHÁLY
Budapest University of Technology
and Economics
Institute of Physics
Department of Physics

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## Introduction

The effect of strong electron-electron interaction, which leads to a tendency towards the formation of various broken symmetry ground states, has been a central problem of the solid state physics in the last half century. Our dc transport and optical studies have demonstrated that electron correlations play a crucial role in each phase of $BaVS_3$.

At ambient pressure this material undergoes a transition from a high-temperature paramagnetic "bad metal" phase to a singlet insulator state at $T_{MI} = 70\,\mathrm{K}$. Suitable microscopic description of these phases can only be provided by involving orbital physics. In the last decade a new type of ordering, called orbital order has been observed in a broadening range of materials, namely in manganese, nickel and vanadium oxides. This phenomenon appears in systems having degenerated orbital levels and results in a periodic pattern of the occupation of the different shaped orbitals over the lattice. Indirect evidences suggest the presence of such an order in the ground state of $BaVS_3$.

## Objectives

The aim of my Ph.D. work was to explore the "magnetic field – pressure – temperature" phase diagram of a vanadium based correlated *d*-electron compound, the $BaVS_3$.

The metal to insulator transition is highly sensitive to the applied hydrostatic pressure. The insulating phase can be completely suppressed by experimentally available pressures and at low temperature a quantum phase transition can be induced. This quantum critical region is manifested in the non-Fermi liquid behaviour of the transport properties. The pressure or composition induced quantum phase transitions are among the hot problems of our days' solid state physics.

The collective behaviour of the electron system is present in every phase of $BaVS_3$, therefore a good understanding of the different states would be valuable for strong correlation physics, in general.

## New scientific results

1. On the basis of the resistivity, thermoelectric power and infrared spectroscopy measurements performed at the ambient pressure in the high-temperature phase of $BaVS_3$, I have demonstrated that the system is situated at the edge of the metallic state with a strong tendency towards localization. Transport and optical properties demonstrate that the electrons have anomalously short lifetime (the mean free path is very close to the lattice constant) and large effective mass ($m^* \approx 7m_{e^-}$) [1, 2]. Conduction anisotropy measurements have shown that the transport mechanism is nearly isotropic [1]. Based on the results of the thermoelectric power experiments I estimated the bandwidth to be $W_{eff} \approx 4000\,\mathrm{K} = 0.34\,\mathrm{eV}$. The on-site Coulomb repulsion for $d$ orbitals is $U \approx 1\,\mathrm{eV}$. Thus the relative strength of the correlation, $U/W_{eff}$ in $BaVS_3$ is close to unity.

2. I have shown that the metal to insulator transition, which occurs at $T_{MI} = 70\,\mathrm{K}$, is of second order at ambient pressure [3]. The argumentation is based on the analysis of the low-field $H - T$ phase boundary determined by magnetoresistance measurements and the comparison of the magnetic susceptibility and specific heat anomalies reported in the literature. This statement has recently got direct evidence by the observation of the structural component of the transition in X-ray experiments.

3. I have explored the $p - T$ phase boundary both by transport and infrared conductivity experiments [4, 5]. For the optical studies I have

developed a pressure cell which is applicable up to 30 kbar and allows investigations also in the long wavelength, far-infrared region. The metal-insulator transition is suppressed under hydrostatic pressure with a rate of $\sim 3.5\,\mathrm{K/kbar}$. The second order transition line extends up to at least $p = 19\,\mathrm{kbar}$, where the transition temperature is reduced to $T_{MI} = 7.5\,\mathrm{K}$.

4. I have proposed that the metal-insulator transition is an orbitally driven spin-Peierls-like transition. The reduced $H - T$ phase boundary of the singlet insulator (when $H$ and $T$ are measured in the units of the zero field transition temperature) is independent of pressure and agrees well with the universal phase diagram of the spin-Peierls systems [3]. The spin gap, which is the order parameter of the singlet insulator, is derived from magnetoresistance measurements as a function of pressure in the range of $p = 0 - 15\,\mathrm{kbar}$ [3]. Its is $\Delta_s \approx 250\,\mathrm{K}$ at ambient pressure and satisfies a scaling relationship: $\Delta_s(p) \approx 3.6 \cdot k_B T_{MI}(p)$, where the scaling factor is close to the BCS value.

5. I have determined the charge gap of the insulating phase both by dc transport and infrared conductivity measurements at various pressures up to $p = 18\,\mathrm{kbar}$ [5]. It is $\Delta_{ch} \approx 750\,\mathrm{K}$ at ambient pressure and it also scales with the transition temperature according to $\Delta_{ch}(p) \approx 10 \cdot k_B T_{MI}(p)$. The charge excitations are of much higher energy than the spin excitations. Their scale is related to the on-site Coulomb repulsion, since they are accompanied with a double occupation on the vanadium sites. In contrast, the energy needed to break up of singlet pairs, which does not necessarily result in double occupancy, is determined by the exchange coupling.

6. At high pressures, when the transition temperature is sufficiently re-

duced, I have observed the magnetic field induced collapse of the second order phase boundary. At $p = 19\,\mathrm{kbar}$, the metal to insulator transition becomes first order at a critical magnetic field of $B_c \approx 6\,\mathrm{T}$. The appearance of a first order phase boundary in the presence of a magnetic field is characteristic of spin-Peierls systems.

7. The insulating phase is completely suppressed at $p = 22.5\,\mathrm{kbar}$ and the metallic state extends to zero temperature. At a certain pressure between $p = 19\,\mathrm{kbar}$ and $22.5\,\mathrm{kbar}$, a quantum phase transition occurs at zero temperature from the singlet insulator to the paramagnetic metal [4, 6]. The quantum fluctuations become strong enough to destroy the singlet phase. In the vicinity of the critical pressure, the fluctuations enhance the electron-electron scattering over an extended range of temperature. This results in a power-law behavior of the resistivity $\rho \propto T^{\alpha}$ with an unusual exponent $\alpha < 2$. In our case $\alpha \approx 1.25$ and the power-law holds from $T = 1\,\mathrm{K}$ to $40\,\mathrm{K}$. Such a phenomenon has been known to be present in systems close a ferromagnetic or antiferromagnetic critical point, but not in a singlet insulator.

## List of publications

### Publications related to my Ph.D. work:


[1] G. Mihály, I. Kézsmárki, F. Zámborszky, M. Miljak, K. Penc, P. Fazekas, H. Berger, and L. Forró
*Orbitally driven spin pairing in the 3d non-magnetic Mott insulator $BaVS_3$: evidence from single crystal studies*
Phys. Rev. B, Rapid Communications **61**, 7831 (2000)

[2] G.Mihály, I. Kézsmárki, P. Fazekas, C. Homes, L. Mihály, H. Berger,

N. Barišić, R. Gaál, L. Forró
*Optical and transport properties in the bad metal phase of $BaVS_3$*
to be published

[3] I. Kézsmárki, Sz. Csonka, H. Berger, L. Forró, P. Fazekas, and G. Mihály
*Pressure dependence of the spin gap in $BaVS_3$*
Phys. Rev. B, Rapid Communications **63**, 81106 (2001)

[4] L. Forró, R. Gaál, H. Berger, P. Fazekas, K. Penc, I. Kézsmárki, and G. Mihály
*Pressure induced quantum critical point and non-Fermi-liquid behavior in $BaVS_3$*
Phys. Rev. Lett. **85**, 1938 (2000)

[5] I. Kézsmárki, R. Gaál, C. Homes, G. Mihály, H. Berger, N. Barišić, L. Forró, and L. Mihály
*Pressure induced suppression of the singlet insulator phase in $BaVS_3$: infrared optical study*
to be published

[6] P. Fazekas, K. Penc, H. Berger, L. Forró, Sz. Csonka, I. Kézsmárki, and G. Mihály
*$BaVS_3$: from spin gap insulator to non Fermi liquid*
Physica B **312**, 694 (2002)

**Additional publications:**

[1] Z. V. Popovic, G. Mihály, I. Kézsmárki, H. Berger, L. Forró, and V. V. Moshchalkov
*Phonon and spin dynamics in $BaVS_3$ single crystals*
Phys. Rev. B **65**, 132301 (2002)

[2] N. Barišić, R.Gaál, I. Kézsmárki, G. Mihály, and L. Forró
*Pressure dependence of the thermoelectric power of single-walled carbon nanotubes*
Phys. Rev. B **65**, 241403 (2002)

[3] J. Balogh, L. F. Kiss, A. Halbritter, I. Kézsmárki, and G. Mihály
*Magnetoresistance of Ag/Fe/Ag and Cr/Fe/Cr trilayers*
Solid State Commun. **122**, 59 (2002)

[4] J. Balogh, I. Vincze, D. Kaptás, T. Kemény, T. Pusztai, L.F. Kiss, E. Szilágyi, Z. Zolnai, I. Kézsmárki, A. Halbritter, and G. Mihály
*Interface magnetoresistance of Fe/Ag multilayers* Physica Status Solidi A **183**, 621 (2002)

[5] F. Zámborszky, I. Kézsmárki, L.K. Montgomery, and G. Mihály
*Pressure induced crossover in the electronic states of $(TMTTF)_2Br$*
Ferroelectrics **249**, 57 (2001)

[6] G. Mihály, I. Kézsmárki, F. Zámborszky, and L. Forró
*Hall effect and conduction anisotropy in the organic conductor $(TMTSF)_2PF_6$*
Phys. Rev. Lett. **84**, 2670 (2000)

[7] G. Kriza, G. Szeghy, I. Kézsmárki, and G. Mihály
*Field scaling and exponential temperature dependence of the magnetoresistance in $(TMTSF)_2PF_6$*
Phys. Rev. B, Rapid Communications **60**, 8434 (1999)

[8] G. Mihály, F. Zámborszky, I. Kézsmárki, and L. Forró
*Dimensional crossover, electronic confinement and charge localization in organic metals*
in Open Problems in Srongly Correlated Systems, Ed. J. Bonca, pp. 263-271 Kluwer Academic Publishers (2001)

[9] J. Balogh, A. Gábor, D. Kaptás, L.F. Kiss, M. Csontos, A. Halbritter, I. Kézsmárki, and G. Mihály
*GMR of a single interface: magnetoresistance of Ag/Fe/Ag trilayers*
in "Kondo Effect and Dephasing in Low-Dimensional Metallic Systems", Ed. C. Van Haesendonck, Kluwer Academic Publishers (2001)

[10] G. Kriza, G. Szeghy, I. Kézsmárki, and G. Mihály
*Power law field dependence of the 2D magnetoresistance in (TMTSF)2PF6*
Journal de Physique IV France **9**, Pr10-235 (1999)

[11] I. Kézsmárki, F. Zámborszky, L.K. Montgomery, and G. Mihály
*Conduction anisotropy of the Bechgaard salts*
Journal de Physique IV France **9**, Pr10-263 (1999)