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DIPLOMA THESIS

Pressure influence on the magnetic and transport properties of the f-electron compounds

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Prohlašuji, že jsem svou diplomovou práci napsal samostatně a výhradně s použitím citovaných pramenů. Souhlasím se zapůjčením práce.

V Praze dne   Martin Míšek

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Abstrakt: V této práci je popsána nová tlaková cela, její uvedení do provozu ve Společné laboratoři pro magnetická studia, současně s testovacími měřeními, nezbytnými pro zajištění kontroly podmínek experimentu a bezproblémový chod. K prvnímu reprezentativnímu měření s novou komorou byl vybrán monokrystal sloučeniny CePtSn. Byl měřen elektrický odpor podél krystalografické osy b za podmínek: T = 2-300 K, p = 0-2.5 GPa a v magnetickém poli B = 0-14 T aplikovaném podél b-osy. Zjistili jsme pouze minimální vliv tlaku na teploty magnetických fázových přechodů, o to zajímavější pak byly výsledky vlivu tlaku na chování v magnetickém poli. V předchozích pracích byly pozorovány dva polem indukované fázové přechody za nízkých tepot (T < 3K) a za normálního tlaku, s hodnotami kritických polí B_c^{LF} ~ 4 T, respektive B_c^{HF} ~ 11.5 T, spojené s významnou změnou elektrického odporu -30% respektive +10%. S aplikací tlaku byl pozorován posun kritického pole dolního přechodu B_c^{LF} směrem do vyšších polí, zatímco horní přechod nebyl tlakem ovlivněn. Za tlaku p ~ 1.5 GPa hodnota B_c^{LF} dosáhla hranice B_c^{HF} a byl pozorován pouze jeden přechod. S dalším zvyšováním tlaku nad 1.5 GPa se obnovila stejná situace s dvěma přechody, jako v oblasti nižších tlaků a B_c^{LF} klesalo s rostoucím tlakem. Při tlaku ~ 2.5 GPa dosáhlo B_c^{LF} hodnoty přibližně 5 T. Výsledky byly porovnány s dřívějšími experimenty.

Klíčová slova: sloučeniny vzácných zemin, vysoké tlaky, elektrický odpor, magnetismus

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Abstract: In this thesis, we describe the work with a new pressure cell, its implementation in Joint Laboratory for Magnetic Studies, together with testing measurements necessary for ensuring good environmental conditions control and trouble-free operation. We have chosen a single crystal of the CePtSn compound to be the first representative measurement. We measured electrical resistivity along crystallographic b-axis in conditions: T = 2-300 K, p = 0-2.5 GPa and magnetic field B = 0-14 T applied along b-axis. We observed only minimal pressure influence on temperatures of magnetic phase transitions, however interesting and rather unusual behavior in magnetic fields was revealed. Previous works reported two field-induced transitions at low temperatures and ambient pressure, with values of the critical fields B_c^{LF} ~ 4 T and B_c^{HF} ~ 11.5 T, accompanied with large magnetoresistence step of -30% and +10%, respectively. With application of pressure, we observed shift of the critical field of low-field transition B_c^{LF} to the higher fields, whereas the value of critical field of high-field transition B_c^{HF} was unaffected with applied pressure. At a p ~ 1.5 GPa the two transitions merged and only one step was observed. With pressure further increasing above 1.5 GPa, situation with two transitions, similar to the lower pressure region, was restored and B_c^{LF} decreased with increasing pressure, reaching the value ~ 5 T at pressure ~ 2.5 GPa. Results were compared to the previous works.

Keywords: rare-earth compounds, high pressure, electrical resistivity, magnetism

1.Introduction

Pressure as a parameter in solid state physics can be helpful tool for investigating physical properties of materials, since a large variety of them depend on interatomic distances or unit cell volume, which can be altered with applied pressure. Application of pressure can lead to change of possible physical states, conditions of phase transitions, magnitudes of effects observed at ambient pressure, etc. It is the alternative way to widely used atomic substitutions (so called "chemical pressure") but it has great advantage because of its pure character.

We can say that high pressure research is a minor part of condensed matter physic. There are still only few very good facilities specialized in high pressure physics, however many others are trying to implement some of its techniques as a useful tool for their own research. Considering the fact that serious high pressure research of material properties started approximately sixty years ago (history of high pressures in solid state physics is very nicely presented in [1] and references therein), it can be a bit surprising that most of the experimental equipment is unavailable commercially and people in this area of physics usually construct it themselves. Another problem is a lack of general theoretical background of physical phenomena under high pressures. For reasons mentioned above, high pressure physics represent a great challenge, but can be rewarded with very interesting and unique results.

Thesis is organized as follows. In chapter 2, theory of physical phenomena concerning this work, is summarized. In chapter 3 we present overview of high pressure techniques together with description of equipment designed and manufactured on our department then follows in second chapter.

One of the main objectives of the presented work, besides better understanding of the physics involved, was to get a deeper knowledge and skills in high pressure experimental techniques. Usually, the experimental equipment is just

briefly introduced. Due to a large amount of time spent with a new pressure cell, attempting to make it work, whole chapter 4 is devoted to it.

In the 5th chapter I will present some recent results of high pressure magnetic and transport measurements on a CePtSn compound, performed after successfully managing to control the experiment. Reasons for choosing just this material for the first measurements lies in its unusual magneto-elastic behavior [2, 3] and thus, it is obviously an ideal candidate for high pressure studies. Experiments were performed in cooperation with the Physical Department of Academy of Sciences of Czech Republic, most of them were carried out in Joint Laboratory for Magnetic Studies (JLMS).

At the end, all obtained results will be summarized and I will mention also our ongoing research and shortly introduce plans for future.

2.Theory

2.1. Magnetic ordering

Magnetic ordering can occur in situation, where interactions of magnetic moments are strong enough to overpower thermal fluctuations.
There are several types of interaction [4, 5]:

1. **Direct exchange** – arises from direct Coulombic interaction between magnetic moments of the neighboring ions. This interaction is strong, but short range. It occurs in compounds containing delocalized (usually d-electron) states.
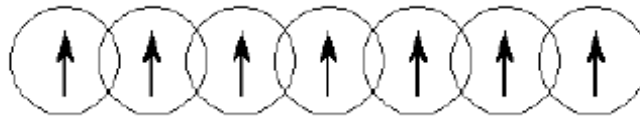
2. **Indirect exchange** – occurs in compounds, where magnetic ions are separated from each other by nonmagnetic ions, via polarization of their ligand states.

3. **RKKY interaction** – this interaction is mediated by conduction electrons. Due to oscillatory character of conduction electron states (bloch waves), it has also oscillatory character and can be responsible for both, ferromagnetic and antiferromagnetic ordering, depending on distance between ions
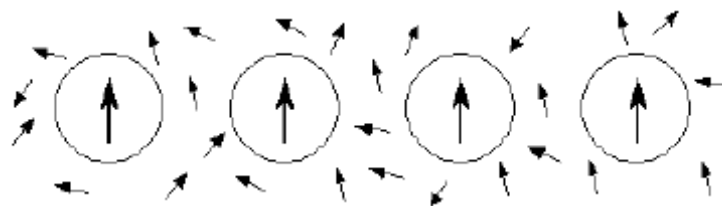
There is also dipole-dipole interaction, but in most cases, it is not taken into account because of the fact, that it is much weaker then exchange and RKKY interactions. However, dipole-dipole interaction is responsible for creation of magnetic domains in the sample.

Magnetically ordered systems can be described by two limiting cases:

1. **Localized moments magnetism** – well describes the system of electrons well localized in real space (as a 4f states of rare earths, for example), which does not contribute to conductivity and chemical bonding. Direct overlap of 4f states of electrons of neighboring ions is negligible, therefore L-S coupling is dominant in this case. Hund's rules are valid and total angular momentum is good quantum number. Magnetic moments are stable with values expected from free-ion model [5].

2. **Itinerant magnetism** – well describes properties of compounds containing electronic states localized in k-space (d-metals), responsible for electric conductivity and chemical bonding. Due to their delocalized (in real space) nature, angular momentum is no longer a good quantum number and magnetism is mainly of spin origin. Conduction electrons form a band structure. Within Stoner model, stable state with spin polarized band structure with non-zero magnetization can be found [6]. Value of magnetic moment per electron is lower than expected from free-ion model.

These models are well understood, however in these days, studied compounds usually contains elements of both kinds, with localized moments (4f-states of lanthanides) and itinerant electrons (d-metals) which makes situation much more interesting and complex.

2.2. Electrical resistivity

The ability to conduct electric current in metallic materials is caused by presence of free charge carriers – electrons. With application of electric field we observe a current in a material proportional to applied field and following its direction. This behavior is described by Ohm's law:

$$I = \frac{U}{R} \tag{1}$$

The finite resistivity is caused by various scattering processes of conduction electrons. Matthiessen's rule says that these scaterring processes can be considered as independent and hence probability of scattering by any of them in one event can be expressed as a sum of probabilities of individual scattering mechanisms. So for total resistivity, we can assume simple additive behavior and deal with individual contributions separately [4]:

$$\rho = \rho_0 + \rho_{phon} + \rho_m \tag{2}$$

where ρ_0 is residual resistivity from scattering on imperfections of crystal structure, ρ_{phon} is phonon scattering and ρ_m is given by a scattering on magnetic moments. ρ_0 is a temperature-independent constant, whereas other contributions are temperature-dependent.

For ρ_{phon}, within the Debye model of lattice dynamics, Bloch-Grüneisen formula can be derived [4]:

$$\rho_{phon} = 4C_{phon} \left(\frac{T}{\Theta_D}\right)^5 \int_0^{\Theta_D/T} dx \frac{x^5}{(e^x - 1)(1 - e^{-x})} \tag{3}$$

For low temperatures ($T<<\theta_D$) it is proportional to $\sim T^5$ and for high temperatures ($T >> \theta_D$) it vary linearly with T, which is in good agreement with experiments.

For the magnetic contribution ρ_m, situation is much more complex and resulting resistivity depends on type of the magnetic structure. However, in the simplest model – neglecting other possible microscopic effects, it can be considered temperature independent above ordering temperature T_{ord} and decreasing with temperature decreasing under T_{ord}, typical scheme is in Fig. 2.1.
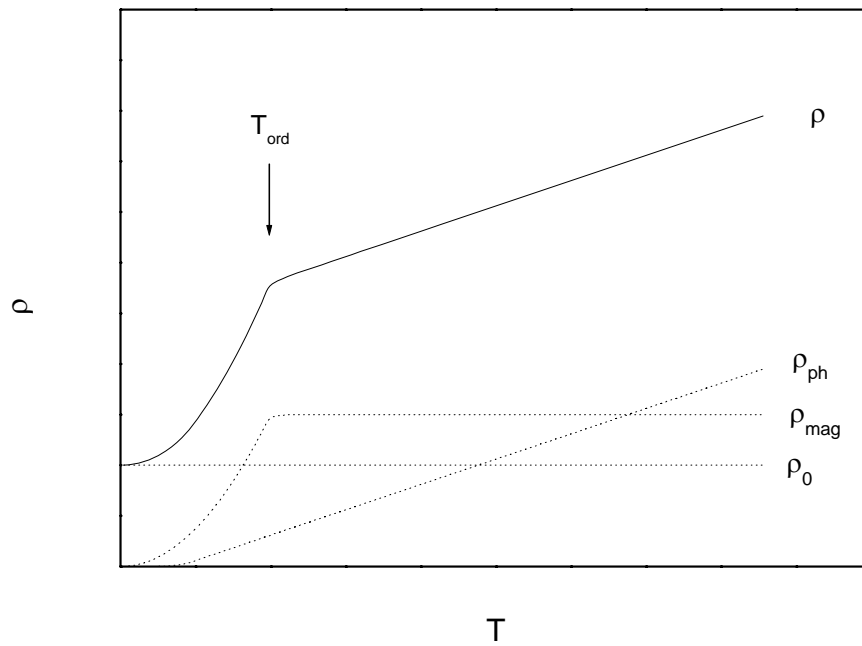

Fig. 2.1. Scheme of typical temperature dependence of electrical resistivity of a metallic material undergoing magnetic phase transition

Magnetoresistence

Magnetoresistence is an effect, when electrical resistivity of material is in some way altered with application of external magnetic field. There are more effects that can be responsible for such a behavior.

With application of external magnetic field, Lorentz force acts on a charge carriers and their trajectory is curved. Resistivity is always increased (except the case of magnetic field parallel to direction of current), this effect being called "normal magnetoresistance".

In magnetic materials, magnetoresistance can be observed when applied field induces change in type of magnetic ordering. This effect originates in different microscopic details of scattering processes on different magnetic structures. It is hard to predict the change in conductivity in such a case without precise theoretical computations but generally more symmetrical magnetic phase will show lower electrical resistance. As an example of systems showing significant MR effects, some well known cases are mentioned in the following paragraph.

Systems of layered structures consisting of ferromagnetic and nonmagnetic layers can be given as very well known example of magnetoresistive material. Coupling between the magnetic layers is governed by RKKY interaction and with proper stacking with nonmagnetic layers it can result in relatively weak AF coupling between them, which can be easily overpowered by application of external magnetic field. This usually leads to significant drop of electrical resistance and effect is called Giant Magneto-Resistance (GMR) [4].

Magnetoresistance can be also realized in systems of magnetic "nanoparticles" separated by thin insulating layer. Tunneling of electrons between particles is also spin dependent and resistivity can change rapidly with increasing field. This effect is called Tunneling Magneto-Resistance (TMR) or Ballistic Magneto-Resistance (BMR) [4, 7].

Kondo effect

Kondo effect refers to interaction of conduction electrons with moments of magnetic impurities. This interaction affects most of thermodynamic and transport properties. As for electric transport, it gives rise to an existence of local minimum in the temperature dependence of resistivity at a finite temperature. Originally, Jun Kondo's calculations lead to divergent behavior with temperature tending to 0 K [6]. Later calculations refined this result to produce a finite resistivity, but retained the feature of the resistance-minimum in non-zero temperature.

A logarithmic term $\rho_{Kondo} \sim \ln(T_K/T)$ can be added to equation (2) to describe Kondo effect on resistivity. The Kondo temperature T_K is defined as the energy scale limiting the validity of the Kondo results.

Pressure effect on magnetic properties

It is hard to find any literature source dealing with influence of high pressure on material properties generally. Concerning only area of magnetism, last attempt to present an exhaustive overview was done more than 30 years ago [8, 9]. Therefore, I will only briefly introduce some of the general ideas concerning magnetic properties and electronic structure under high pressures.

Generally, change of electronic structure with decreasing volume, can be thought as a continuation of changes related to the transition from isolated atom to the solid state. The most sensitive to the volume changes are outer electrons. The decrease of interatomic distances causes an increase of their interaction with nuclei, inner electrons and with the outer electrons of neighboring atoms. The most significant change is the increase of overlap integral of wave functions of electrons

of the neighboring atoms, which leads to further delocalization of electrons, broadening of the energy bands and a possible change of character of chemical bonding (ionic → covalent → metallic). At extremely high pressures (1 TPa and more), the inner electrons can be delocalized too and an atomic shell structure can be destroyed entirely. Such a change is accompanied with gradual decrease of the magnetic moment to possible extend of complete suppression of magnetism at sufficiently high pressure. However, pressure needed for such a scenario is far beyond our experimental possibilities. In pressure range achievable with our equipment, altering the direct exchange interaction usually leads to observable decrease of magnetic moment and significant change of ordering temperatures within the itinerant magnetism model. In the localized magnetism model, pressure induced volume changes are usually too low to affect direct overlap and pressure dependence of values of magnetic moments can be considered negligible. Changes of the magnetic properties can be attributed mainly to the altering of some of the indirect interactions.

However, Yb and Ce can be presented as a counterexample of behavior mentioned above. The Yb can acquire a magnetic moment at pressure high enough for removing of an electron from the completely filled 4f shell. The Ce ion can be either in trivalent or tetravalent state in many compounds. Application of high pressure then influences the valence state and a suppression of magnetic moment can occur in this case too [8].

3. Experimental methods

3.1. Overview of high pressure experimental techniques

High pressure experimental techniques can be divided into two groups: statical and dynamical. Dynamical techniques involves short pulses of extremely high pressures caused either by impact of high velocity projectile on a plate with attached sample or by use of explosives. Besides extremely high requirements for safe performance of measurements, these techniques are also difficult for synchronization of all steps of experiment, data acquisition and precise determination of environment conditions.

Main idea of static high pressure technique is having a sample closed in some chamber filled with suitable pressure transmitting medium and act with a force (piston) on a surface of a medium, which leads to hydrostatic pressure inside a chamber. There are two basic types of construction of high pressure cells: piston - cylinder cells and diamond anvil cells (DAC).

There are only few companies offering commercially manufactured high pressure cells (EasyLab [10], Almax-Industries [11]), but most of a high pressure physicists creates their own cells more suitable to the specific requirements of their experiments.

While designing a pressure cell, one must choose the type of cell, construction materials and a way for pressure determination according to the type of experiment. There is always a compromise between maximal achievable pressure and volume of sample (important for e.g. neutron diffraction).

Used materials have to maintain good mechanical properties in desired temperature range and fulfill further requirements according to the type of experiment. For example: nonmagnetic for experiments in magnetic fields, transparent for optical measurements. For diffraction measurements the construction should allow sufficient angular range for incident and diffracted beam, etc.

Same criteria have to be considered to choose proper pressure transmitting medium too. For example: electrically insulating (resistivity), nonmagnetic (magnetization), low absorption (optical, diffraction). Generally, all types (gas, liquid, solid) of pressure transmitting media are used in different types of experiments. Most common are gases and liquids. Gases (e.g. He) are great for creating pure hydrostatic pressure, however, compression energy is rather high. Together with complicated sealing of the cell it makes them not easy for handling and safe performance of experiment. Creating hydrostatic pressures with liquid pressure transmitting media is also possible and they are much more comfortable to use. Their use is limited by theirs solidification at some pressure. It has a character of glassy transition. Since it behaves as a glass above the transition, it can be a bit problematic to create hydrostatic pressure. This problem, considering our experimental setup, is discussed in chapter 3.

Except for widely used oils, there are also other options. Ethanol-methanol, pentan-isopentan mixtures can be used for much higher pressures, but they have many other "user-hostile" properties (flammable, not easy to seal of, chemically aggressive).

Detection of pressure

Originally, pressure was determined by direct measurement of the load on the piston and its area. Considering theoretical models of friction between the piston and rest of the apparatus and assuming no shape change of all parts, pressure could be determined very precisely up to several GPa [12, 13]. These measurements required large pressure cell, not suitable for most of experiments today. Moreover, with construction of devices to higher pressures these measurements became not reliable.

After depleting options of direct measurements, people started to look for another ways. At this place I would like to mention success in evaluating equations of state of some simple systems (e.g. NaCl, Rh) and theoretical description of pressure wave propagation in the dynamical high pressure techniques [12, 13]. Both methods gave reasonable base for creating pressure scale at range ($\sim 10^2 - 10^3$ GPa). There comes obvious question: How treat intermediate pressures?

In most of the crystalline materials some structural changes occur with application of high pressure. Some of them (e.g. Bi I-II, freezing of mercury [8, 13]) were chosen as fixed points at a pressure scale. Today's generally accepted pressure scale was created by combination of techniques mentioned above to pressures up to ~ 10 TPa, however discussion about its reliability and possible extension to even higher pressures still takes place.

For simplicity of experiments, so called secondary pressure gauges are used. They are based on change of some physical properties of materials under applied pressure. Pressure induced shift of luminescence lines of ruby is widely used in DAC experiments as well as structural changes of some materials in diffraction experiments. Among many others, change of critical temperature of transition from normal to superconducting state of Pb and pressure induced change of resistivity of manganin are widely used too. These two detection methods will be discussed in detail in chapter 4.

3.2 Pressure cells designed on our department

In this chapter I will briefly introduce pressure cells designed and manufactured on the Physical Department of ASCR (J. Kamarád). We have two types of hydrostatic pressure cells. First of them is used for magnetization and AC susceptibility measurements in SQUID magnetometer, the other one for resistivity measurements in close - cycle refrigerator (CC). They are depicted in Fig. 3.1.and Fig. 3.2., respectively.
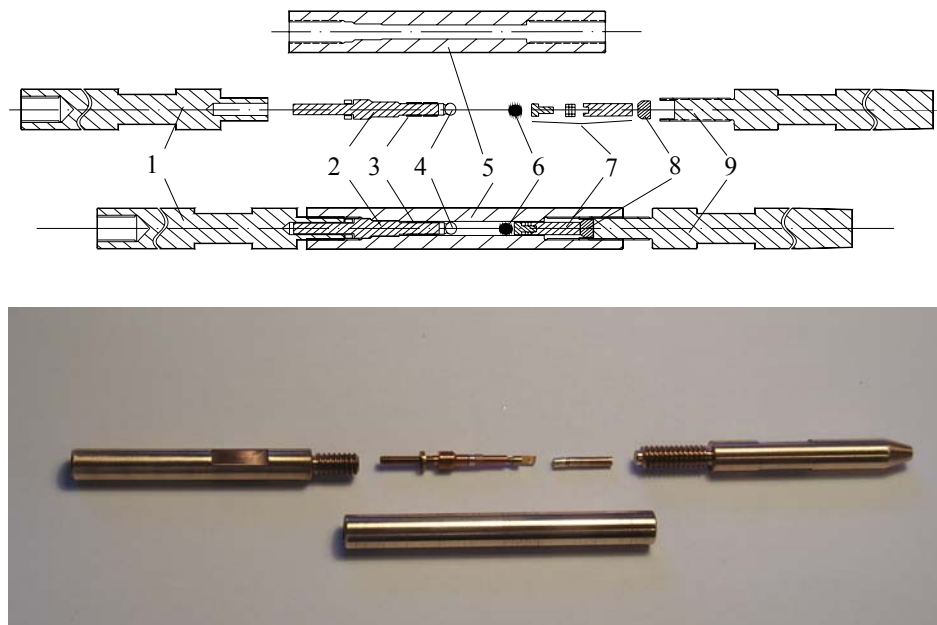

Fig. 3.1 High pressure cell for SQUID magnetometer

1, 9-clamping bolts, 2-plug, 3-sealing rings, 4-sample holder with sample,
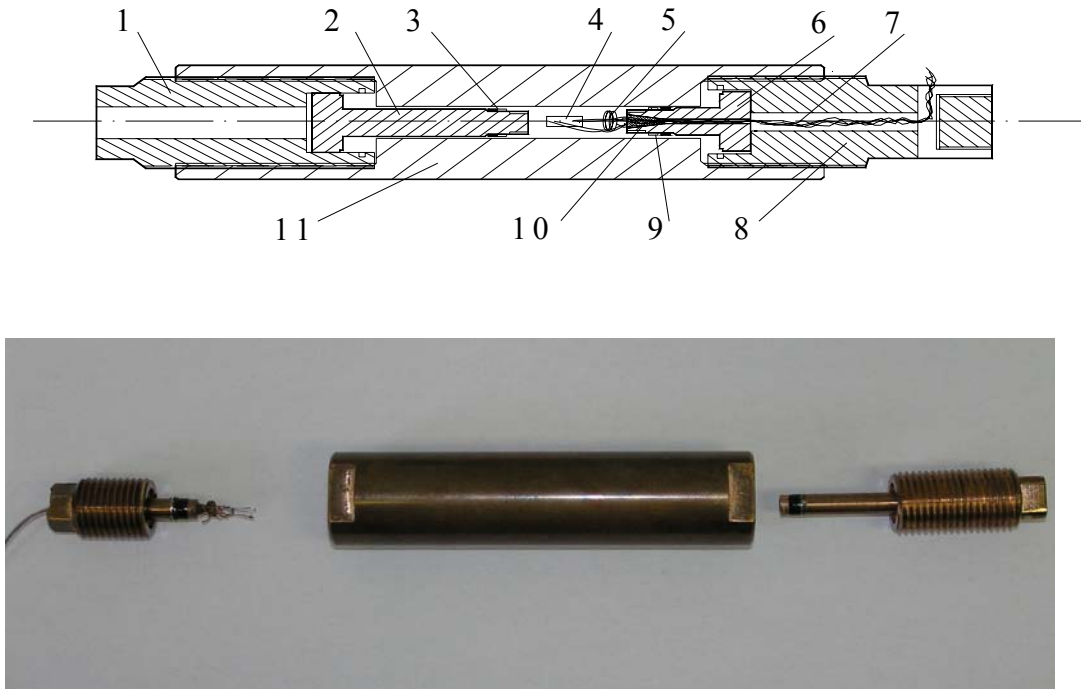5-body of the cell, 6-Pb sensor, 7-piston, 8-support of the piston,

Fig. 3.2 High pressure cell for close - cycle refrigerator

1, 8-clamping bolts, 2-piston, 3-sealing rings, 4-sample, 5-manganin detector,

6-plug, 7-wires, 9, 10-sealing rings,11-body of the cell

Both of them are made of diamagnetic Cu-Be alloy with spindle oil OL3 used as a pressure transmitting medium. Pressure limit for these cells is approximately 1 GPa. As a pressure sensor we use manganin coil (CC) and a shift of Pb superconducting transition (SQUID).

The last of our cells, recently constructed, is a pressure cell for magnetic measurements under uniaxial pressures in SQUID magnetometer. Its design is based on previous hydrostatic SQUID cell. On the outside they look practically the same. Inside, there is a set of ZrO ceramic blocks and disc springs instead of area for sample and oil. Desired pressure is created by fixing the screws into a proper position. The cell is shown in Fig. 3.3.
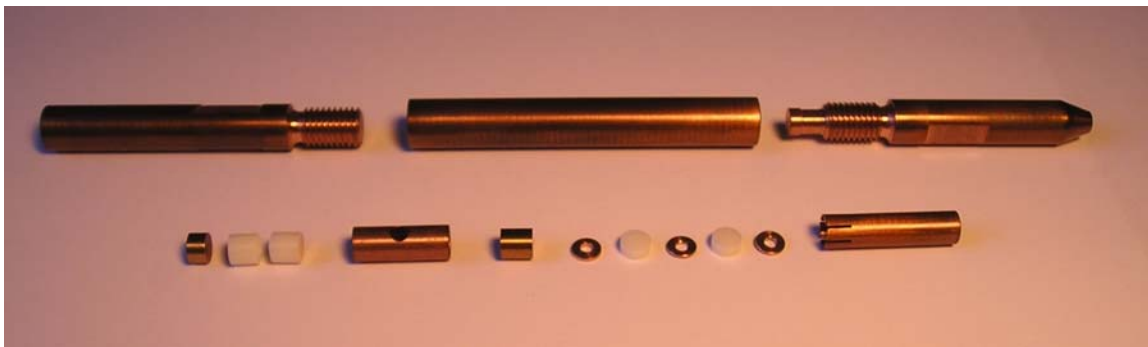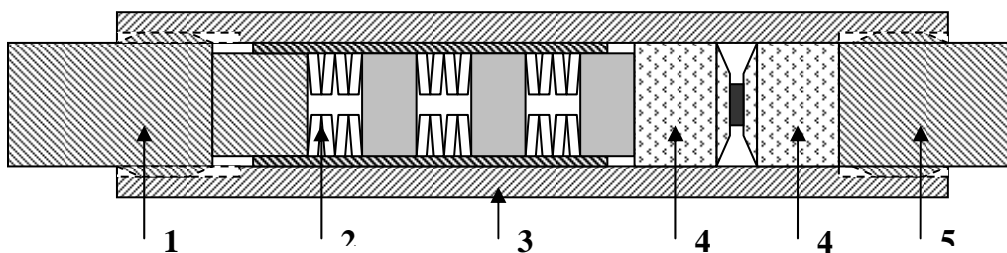

Fig. 3.3. Cell for uniaxial pressures for measurements in SQUID

1, 5-clamping bolts, 2-disc springs, 3-body of the cell, 4-ceramic blocks,

4. New pressure cell

Recently, a piston - cylinder cell for use in Physical Properties Measurement System (PPMS, Quantum Design) was bought on our department. There were some troubles with preparing cell for measurements and has been made a decision about assigning this problem as one of the priorities of my work.

Since this pressure cell is too large for PPMS detecting coils set for magnetic measurements, it is primary meant for resistivity measurements only. The other physical properties we are interested in (magnetization, AC susceptibility, specific heat) are measured by proper conversion of observable to electric signal and thus all these measurements under pressure are possible to perform with the new cell in PPMS too. This requires that we have to prepare our own detection system small enough to fit inside the cell. These experiments are currently in progress and there is still lot of work to do, therefore I will mention some details only in final chapter of this work.

In this chapter I will focus on description of the cell, its function and first testing measurements. The cell is depicted in Fig. 4.1.

Fig. 4.1 The new pressure cell (from left to right): Puck for connection with PPMS, clamping bolt, plug, sealing rings and a Teflon capsule, body of the cell, piston, clamping bolt

Description

This cell uses a type of construction where main body of the cell consists of two parts. The outer cylinder (as well as the plug and outer screws) is made of Cu-Be alloy. Inner cylinder is made of Ni-Cr-Al alloy. Outer diameter of inner part is slightly higher than inner diameter of outer part. In the construction process they are put together either by cooling inner cylinder, and pushing it into the outer one or both interfaces are in shape of cone (angle ~1°) and the inner part is pressed into the outer one. This type of construction creates some initial stress at the interface, which leads to higher achievable pressure inside the cell.

Sealing of the sample area is realized by teflon capsule together with two Cu-Be rings at both sides. Twelve 100 μm Cu wires are sealed in the plug using Stycast epoxy and Catalyst 9 hardening agent (Emerson & Cuming). For our measurements 8 wires are enough, but after having occasionally trouble with damaging some of them during preparation of the plug I decided to put some extra wires just in case.

Sample is usually in a tetragonal shape of about 1x1x5 mm. 50 μm silver wires are attached on sample either with a colloidal silver solution or with a special electrically conductive epoxy and on the other end soldered to the wires coming through the plug. All connections are sealed with insulating glue to avoid electrical contact in case of shift of the wires during pressurizing the cell.

At the beginning we had problems with sealing the wires in the plug. How trivial this problem may seem to people unfamiliar with high pressure research (principle is simple, it does not include solving any new physical or technical problem), it is essential for further work with the cell. Wires leading through the plug are experiencing huge pressure gradient. Moreover, the plug can only be used in one pressurizing cycle and is irreversibly damaged during disassembling the cell, therefore requirements for patience and skills of the experimentalist, to ensure high

quality and reproducibility of measurements, are really enormous. After relatively long time spent with solving this problem I finally managed to control the preparation of all parts of the cell at a routine level. Up to date, we performed about 10 successful pressurizing cycles (after about the same number of unsuccessful) and have not encounter any other problems of this kind.

As a pressure transmitting medium we use Daphne[©] oil. Since it is commercial product, it is hard to find out exact composition, but some informations are available [14, 15]. It is a mixture of oils with different chain lengths, where each of them alone undergoes glassy transition at bit different pressure (~1.5 GPa). This leads to more "broadened" transition with gradual change of the volume in the final mixture. Above the transition, it behaves as a highly viscous liquid. It means if we increase load on a piston really slowly to let the shear stress relax, we can achieve hydrostatic pressures also above the glassy transition of the pressure transmitting medium. We do not have any direct measurement of the components of stress tensor to support this conclusion. However measurements of resistivity of manganin indicate that no considerable uniaxial component of pressure is present. Resistivity of manganin is highly sensitive to its plastical deformation and the material is relatively soft. In case of uniaxial squeezing along the piston axis, irreversible change of resistivity should occur. But it wasn't observed. After a pressure cycle with unloading the cell, resistivity of manganin always returned to its original value. For those who are perfectionists this may not be satisfying conclusion, but it is only thing we can at the moment honestly say about this problem.

Pressure determination

Next problem we had to solve was determination of pressure inside the cell. For practical reasons ideal choice for our experiments would be using of manganin coil as a pressure sensor as we do it with our older cells up to 1 GPa. The reliability of manganin in this pressure range (up to 3 GPa) is not a question, there is already enough evidence for using manganin as a sensor to even higher pressures in the literature [13], including nonlinear corrections to linear law at higher pressures. Important question was also a difference between pressure at room temperature and pressure in low temperatures, which we are usually interested in. For this purpose, measuring the shift of the critical temperature of transition of Pb (or another similar standard) from normal to superconducting state was straightforward. For experiment we used 6N pure Pb and a manganin wire calibrated against mercury freezing point, both available in our laboratory. For first set of measurements we used sample of typical dimensions for this experiment (~ 1x1x5 mm). But due to low residual resistivity ratio (RRR) of pure Pb, obtained signal was too low compared to the noise. Transition was observable and T_{sc} shifted with pressure as expected, but to show more representative data I prepared sample with much lower cross-section (~ 0.1x0.3x10 mm) to increase the signal and repeated the measurement. Results are shown in Fig.4.2.
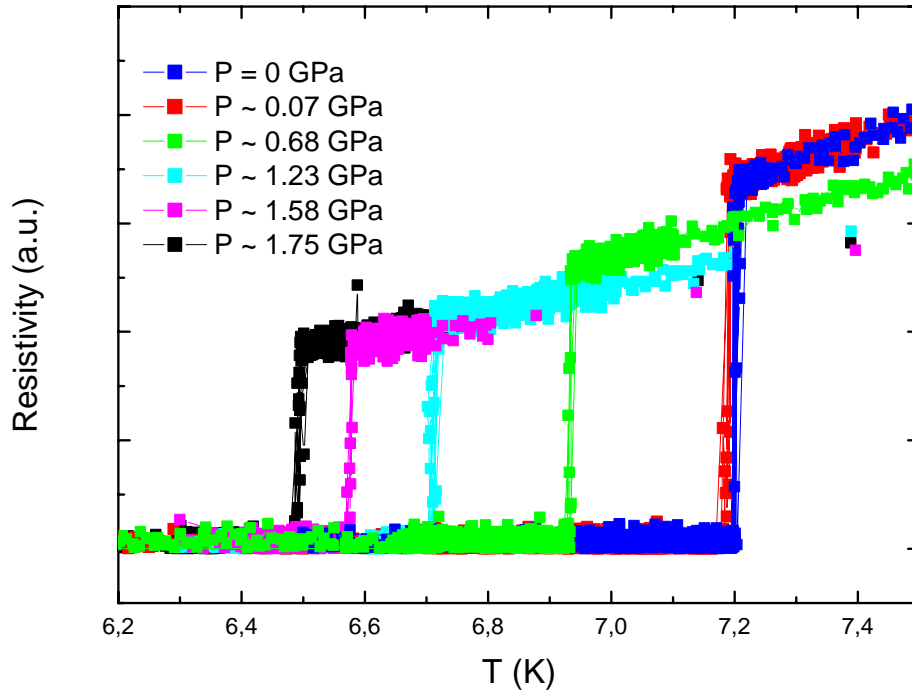
Fig. 4.2. Temperature dependence of the resistivity of Pb pressure standard, pressures are derived from T_{sc} of Pb sample

There are few more details to discuss about this experiment. Considering very low critical field of Pb, one needs to have as low and stable field (ideally zero) as possible.

Superconducting magnet of PPMS is made of NbTi type II superconductor. Even after canceling all macroscopic currents, there is still some superconducting vortex state. Only option for certainty of removing the residual field is heating up the whole magnet above its critical temperature, which is extremely unpractical and expensive. After discussion with more experienced colleagues we performed procedure to minimize this effect [16]. Basic idea is to set the field to zero using oscillation mode of PPMS [17] from some higher field (~ 1 T), wait approximately 1-2 hours and repeat setting zero field and a time delay again.

Typical relaxation times of vortex state decay are of order ~1 h. The resulting residual field of the magnet will not be zero (typically up to ~ 10 Oe [14]), but it will be sufficiently stable.
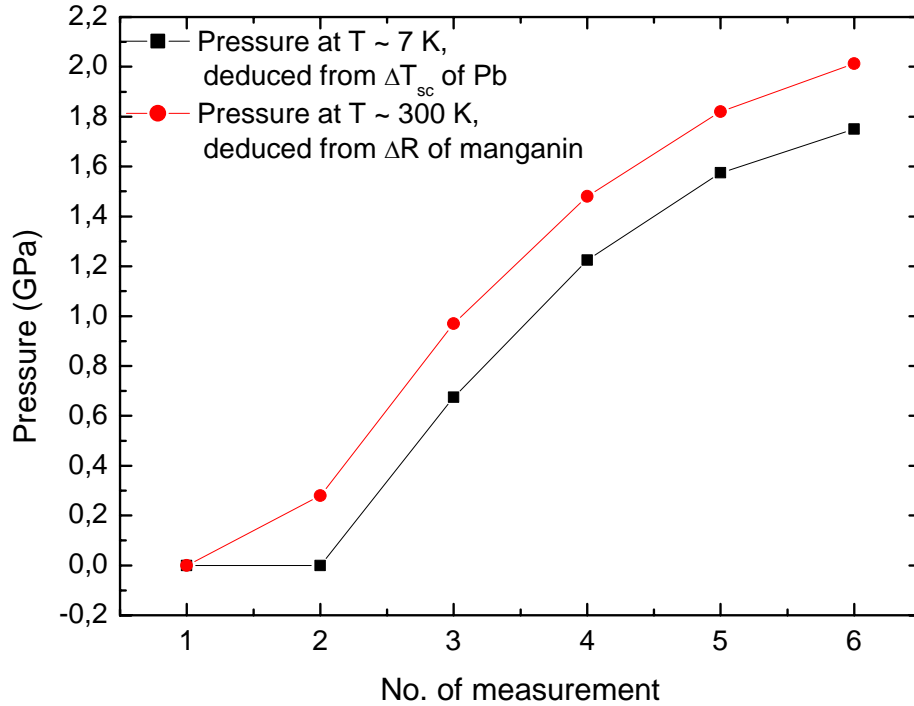

Fig.4.2. Comparison of pressure deduced from resistivity of manganin at room temperature with pressure deduced from change of T_{sc} of Pb sample

To get a sufficiently strong signal, we have been forced to use rather high current I = 20 mA to measure electrical resistivity of the Pb sample. This caused problems with stabilization of temperature in the vicinity of transition to superconducting state. For pressure evaluation we deduced T_{sc} from data obtained during heating the sample. This approach can by justified by absence of Joule heating in the sample in superconductive state and therefore these data can be considered more reliable.

Although we can not determine precisely T_{sc}, due to stability of the residual field we can determine dT_{sc}/dp with sufficient accuracy using measurement with unloaded cell as a reference point. Considering all facts mentioned above, we can estimate the precision of pressure determination $\delta p \sim 0.02$ GPa and a difference of pressure between room temperature and low temperatures (Fig. 4.2.) ~ 0.3 GPa.

5. CePtSn

5.1. Introduction and previous results

The CePtSn compound crystallizes in the orthorhombic TiNiSi-type structure (Pnma space group, Fig. 5.1.). In zero magnetic field it undergoes two magnetic phase transitions, one connected with onset of an antiferromagnetic ordering at temperature $T_N \sim 7.5$ K and the other is a transition between two incommensurate AF phases at $T_t \sim 5.5$ K. Resistivity measurements showed a minimum at $T \sim 30$ K, this behavior was attributed to the Kondo effect. Due to large Ce-Ce atomic distances (3.8292 Å, [3]), only the RKKY interaction is considered to be responsible for magnetic ordering in this compound [3].
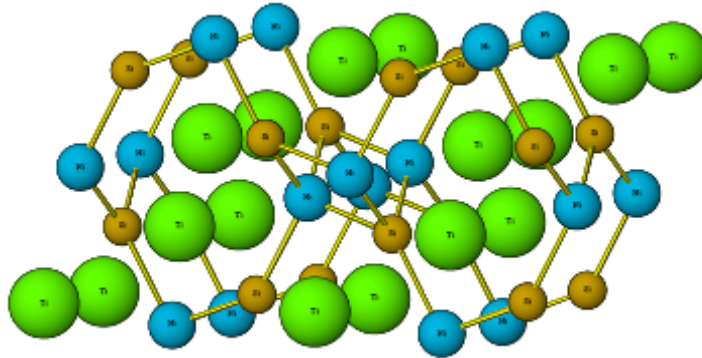

Fig. 5.1. Crystal structure of CePtSn (Pnma space group)

As a next step in the investigation of the properties of this compound, measurements of magnetostriction, magnetoresistance and neutron diffraction under applied magnetic field were performed. All types of measurements revealed highly anisotropic behavior, detailed description of observed phenomena can be found in [2].

The easy axis of magnetization is a-axis (1.2 μ_B/f.u. at 35 T [3]), the c-axis was identified as a hard magnetization axis. For purposes of this work I will introduce only behavior for magnetic field applied along crystallographic b-axis, for which most interesting behavior in the magnetic field was reported. At low temperatures ($T < 3$ K) two field-induced (AF to AF) transitions were observed at field of $B \sim 3.5$ T and $B \sim 11$ T, respectively. Both transitions are accompanied with large magnetoresistence step, -30% and +10% respectively, however, showing only minor features on magnetization curve. Low temperature neutron diffraction data indicated coexistence of two types of AF domains with propagation vectors $q_1 = (0,0.466,0)$ and $q_2 = (0,0.418,0)$ at temperature $T = 2$ K [2], however, with no conclusion about moment directions. With applied field, intensity of q_1-related peaks decreased and vice versa (Fig. 5.2.). Originally, the low field transition was reported as irreversible and zero field cooled state was fully restored only after heating well above 3 K. Suppression of one type of the domains with increasing field has been considered as a possible explanation of observed behavior [2, 3].
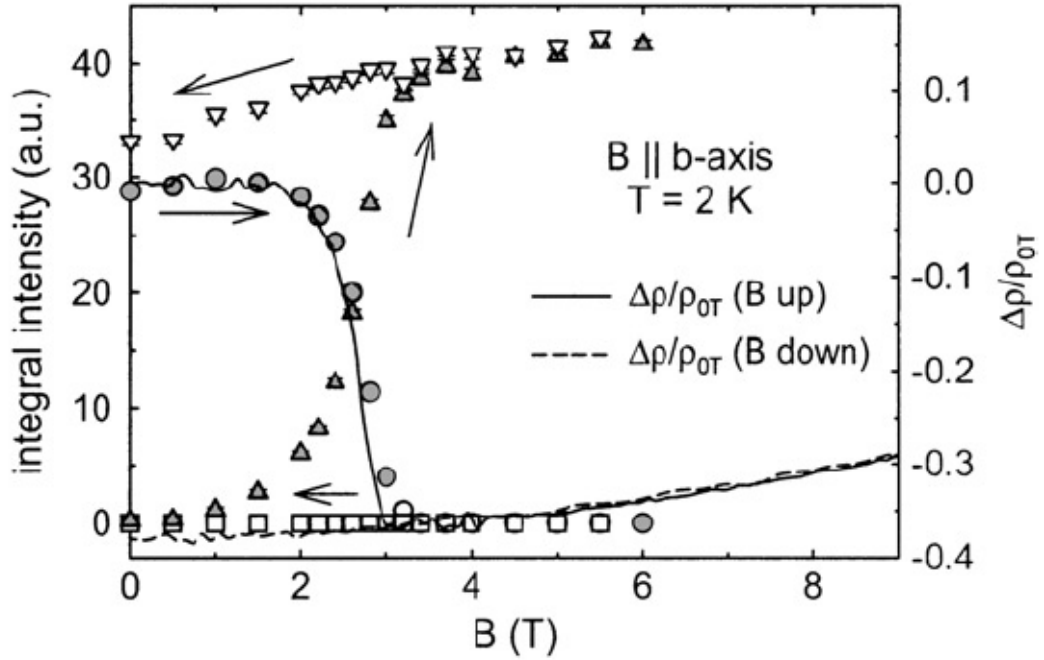
Fig. 5.2. Magnetoresistance and a field dependence of the integral intensity of the two propagation vectors (scaled to fit the magnetoresistance), triangles correspond to q_1-related reflection, squares and circles corresponds to q_2-related one [3].

Effects of Ni substitution for Pt have been also a subject of study [18, 19]. It has been reported that unit cell volume decreases monotonically with nickel doping. The loss of magnetism occurred with Ni concentration ~70% which corresponds approximately to 1.5% volume change. Consequently, high pressure magnetization measurements were performed to further study of volume change influence on magnetic properties of CePtSn in a pure way. The DC magnetization in temperature range 2-300 K and pressures up to 0.82 GPa were carried out in a commercial SQUID magnetometer. The values of transition temperatures T_N and T_t has not shown any significant change with applied pressure. However, decrease of the moment (~25% at 0.82 GPa) was observed [3]. That was considered as a

precursor of suppression of long-range order under considerably higher pressures [3].

These results indicated that hybridization of Ce 4f states with conduction electrons is not strong enough in this pressure range to allow the Kondo effect to overpower the RKKY interaction. As a conclusion from comparison with studies of $CePt_{1-x}Ni_xSn$ series [16, 17], (namely the difference in lattice parameters of CePtSn and CeNiSn, $\Delta a/a$ = +2.05%, $\Delta b/b$ = -0.6%, $\Delta c/c$ = -5.24%, [19]) Ce-Ce interatomic distances, not a unit cell volume, were considered mainly responsible for hybridization strength [3].

5.2. Results

With successful implementation of new pressure cell in the PPMS in our laboratory, we have chosen a CePtSn to be first compound to investigate. Beside an obvious reason for interest for high pressure study coming from previous results, we had an advantage of already possessing the high quality single crystals of CePtSn in our laboratory [2, 3].

We performed the electrical resistivity measurements in PPMS using standard four-probe method at temperatures down to 2 K in magnetic fields up to 14 T and pressures up to ~ 2.5 GPa. Pressure was determined by a resistivity change of manganin at room temperature. Temperature dependence of resistivity under various pressures and a detailed plot in low temperature region of the same dependences are shown in Fig. 5.3. and Fig. 5.4., respectively.
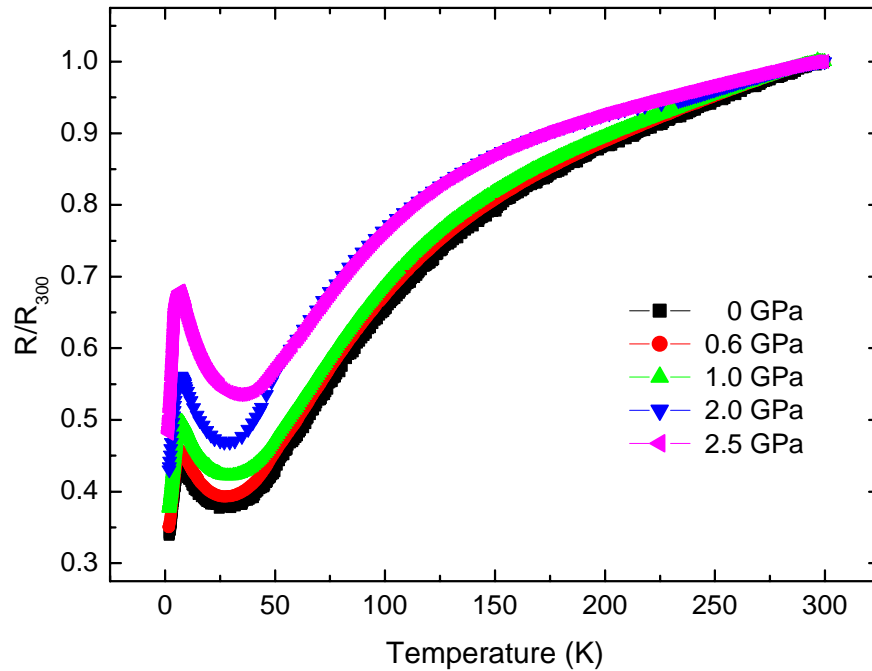

Fig. 5.3. Temperature dependence of the resistivity of CePtSn for various high pressures and zero magnetic field.
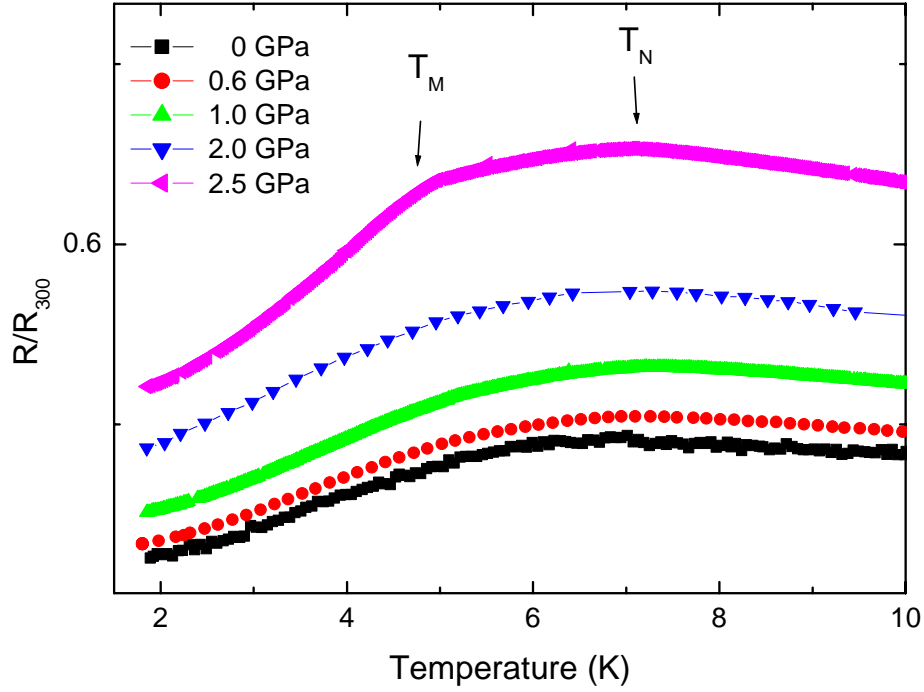
Fig. 5.4. Low temperature detail of the temperature dependence of resistivity of CePtSn, arrows indicates temperatures of the magnetic phase transitions

We concentrated our efforts on studying field induced transitions at low temperatures and a magnetic history dependent phase. With applied hydrostatic pressure the low field transition (LF) is shifted to higher fields at a rather high rate ~ 6 T/GPa. Contrary to results at ambient pressure, this transition become reversible at any applied pressure, however, it shows a large hysteresis. The high field transition (HF) remains almost unaffected by applied pressure, both in position (~ 11.5 T) and magnitude of a MR step. With increase of applied pressure critical field of the LF transition approaches the B_c^{HF} and at a pressure ~ 1.5 GPa only one step-like transition is observed at field ~ 11.5 T, accompanied with a negative magnetoresistence step, but no hysteresis.

With pressure further increased, situation with two transitions similar to lower pressure region is restored at pressure ~ 1.6 GPa and B_c^{LF} is decreasing, reaching ~5 T at 2.5 GPa, whereas B_c^{HF} remains stable in this pressure region too. Obtained data of magnetoresistance at various pressures are shown in Fig. 5.5.
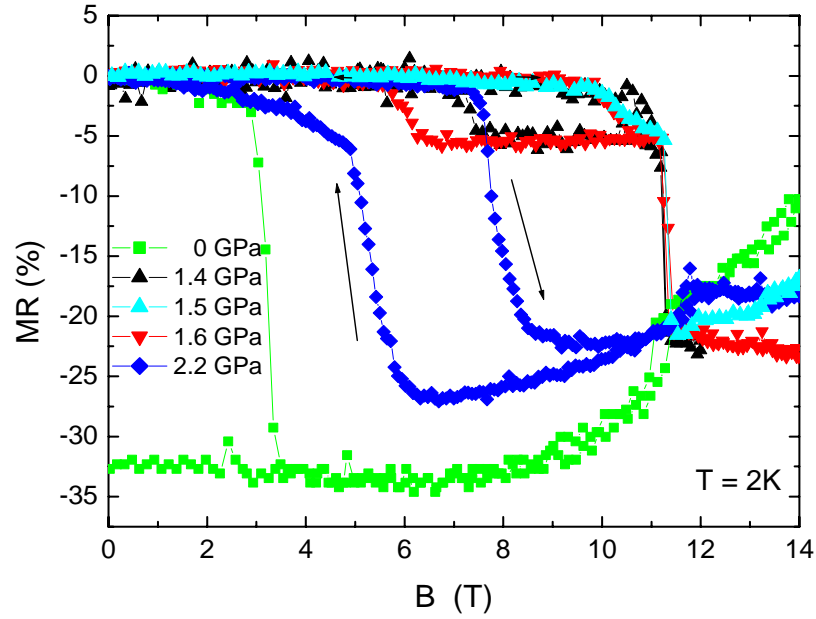

Fig. 5.5. Magnetoresistance of CePtSn at temperature T = 2 K,
for various high pressures

Previous works concluded a major role of the RKKY interaction on behavior of CePtSn compound [3]. We can support this idea with our results, namely with presence of maximum in pressure dependence of critical field of LF transition (Fig. 5.6.).
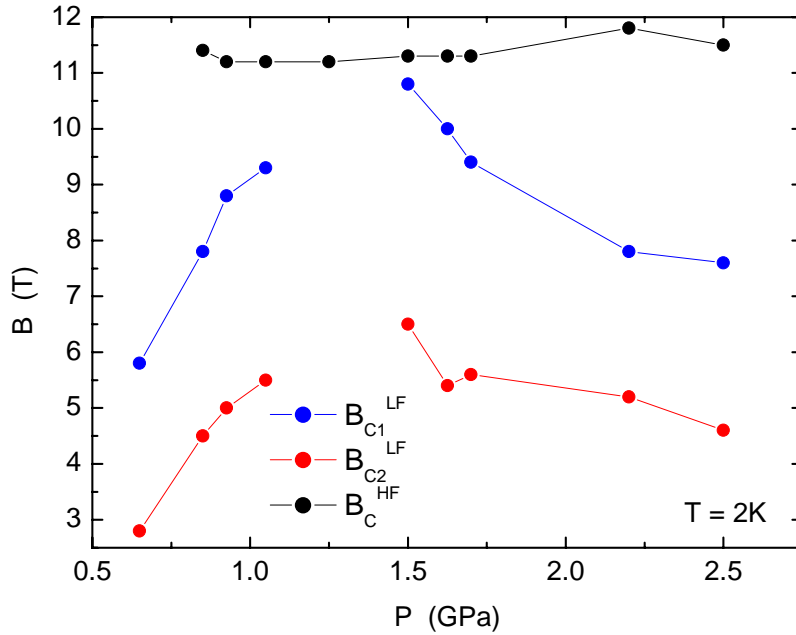
Fig.5.6. Pressure dependence of critical fields as determined from the field dependencies at 2 K. B_{c1}^{LF} indicate the lower transition field observed with increasing field, B_{c2}^{LF} observed with decreasing field, respectively.

For changes of a magnitude of a magnetoresistance step associated with LF transition (Fig. 5.7.), we can assume that ratio of different types of AF domains building a ground state is significantly changed with pressure. However, exact mechanism which would explain in detail observed pressure dependence of MR step, remains unclear.

For more satisfying conclusions in this matter, further work is necessary. Namely application of uniaxial stress and microscopic studies (e.g. neutron diffraction) under hydrostatic pressure could be of significant help.
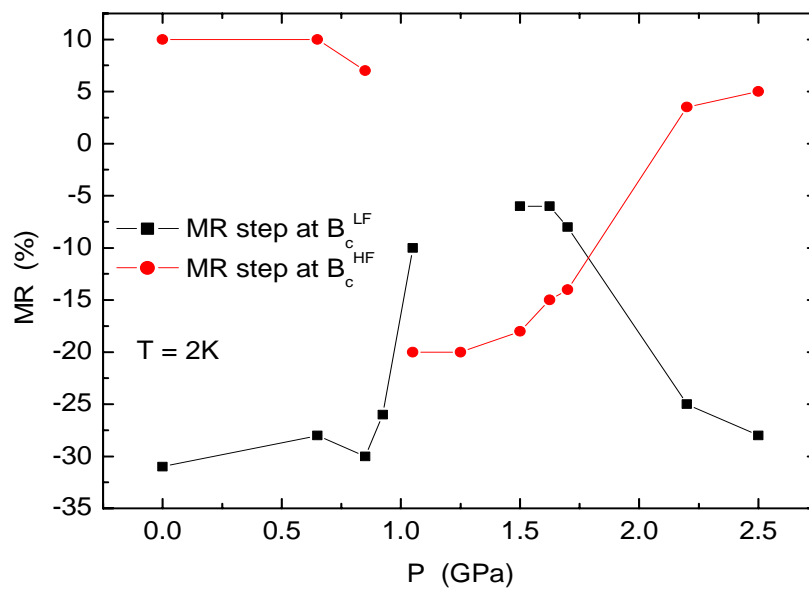
Fig. 5.7. Pressure dependence of resistivity changes accompanying the field induced transitions.

6. Summary, conclusions and outlook

We successfully implemented a new High pressure cell for measurements of electrical resistivity in PPMS in Join Laboratory of Magnetic Studies (JLMS). We carefully carried out testing measurements of electrical resistivity of manganin and Pb to shed some light upon the usability of manganin as a pressure sensor in our experiment. With data provided from our measurements, we were able to determine change of pressure between room temperature (~300 K) and low temperatures (~ 7 K) and estimate a precision of pressure determination.

We measured electrical resistivity of CePtSn compound in environment conditions: T = 2-300 K, B = 0-14 T applied along crystallographic b-axis and p = 0-2.5 GPa. We have not observed any significant pressure effect on the transition temperatures T_M and T_t, nor the position of the minimum in temperature dependence of resistivity.

However, significant and rather unexpected influence of pressure on field-induced transitions at T = 2 K was revealed. We observed a gradual increase of the critical field B_c^{LF} of the first transition (the second transition at B_c^{HF} remains intact) up to ~ 1.5 GPa in which only one transition is observed at ~ 11.5 T. In pressures above 1.5 GPa we observed the two transitions again and B_c^{LF} decreases with further increasing pressure to reach B_c^{LF} ~ 5 T at 2.5 GPa. We can attribute this effect to the pressure induced modification of RKKY interaction in agreement with conclusions of previous works [3] about its major role on properties of this compound.

There are also few more experiments currently in progress. For susceptibility measurements under pressure, we tried to build a detection coils system, small enough to fit inside a new pressure cell. It consists of a primary coil and two secondary coils. Testing outside the cell gave us reasonable results, but the influence of pressure on its behavior is still an open question. So far, we had some success, but the technology of preparing the well balanced coil set will require

further improvements to ensure reliable results. Recently, we found out, that specific heat under pressure could be possibly measured using the AC calorimetry method [20, 21]. In PPMS specific heat (at ambient pressure) is measured by means of co called relaxation method. In this method sample, weakly connected to the heat bath, is slightly heated and then a time of relaxation to the bath temperature is measured [17]. For this case it is also possible to design a small pressure cell, but usability is very limited due to dominant contribution from a pressure cell itself. In the AC calorimetry technique, a heater powered with AC current is attached on the one end of the sample and temperature is measured on the other end. Assuming thermal equilibrium between sample and thermometer, simple formula connecting specific heat of the sample with heating power, strength of heat connection of the sample to the surrounding, frequency of heating and temperature measured with thermometer, can be derived [20].

This experiment is still in the phase of preparation and there are some serious questions to be answered. Namely we are concerned about properties of thermometer and effect of pressure on it. Further problems arise from the comparable size of thermometer and sample (validity of the model) and presence of pressure transmitting media (damping of the signal).

7. References

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