October 2016
No.2016-019-e

Journal of Integrated Creative Studies

Report on my research at the SSPC Laboratory, Division of Chemistry, Graduate School of Science, Kyoto University

Herwig Michor
Institute of Solid State Physics, TU Wien, 1040 Wien, Austria
E-mail: michor@ifp.tuwien.ac.at

Abstract. This report reviews my research conducted as Visiting Fellow at the Solid State Physics and Chemistry (SSPC) Laboratory in the Division of Chemistry financed by the International Research Unit of Advanced Future Studies at Kyoto University. The subject of my research are electronic ground state instabilities and quantum critical phenomena in strongly correlated electron systems, especially those among inter-metallic rare earth compounds. Thereby, two classes of materials are in the focus of my present work. Studies of materials near an itinerant magnetic instability: nearly and weakly ferromagnetic compounds and the characterization of their spin-fluctuation features and magneto-volume effects. The second focus is on cerium and ytterbium based metals with electronic ground state instabilities being related to the mechanisms of Kondo- and/or magnetic frustration effects. Future collaboration plans of the SSPC Laboratory with me and my collaborators at TU Wien are finally outlined, also targeting interdisciplinary research with additional partners.

Keywords: Strongly Correlated Electron Systems, Electronic Ground State Instabilities, Itinerant Magnetism, Spin-fluctuations, Kondo lattice

1. Scientific Activities

My research as Visiting Fellow at the SSPC Laboratory, Division of Chemistry, Graduate School of Science, Kyoto University, was conducted from August 1st to November 30th 2016 in collaboration with Professor Yoshimura, Assoc. Prof. Ueda, Assist. Prof. Michioka and their team of PhD, MSc and undergraduate students. During the first two months (till submission of this report), I had opportunities to discuss with Professor Yoshimura scientific problems of itinerant magnetism as well as of cerium or ytterbium based strongly correlated electron materials and nuclear magnetic resonance (NMR) techniques. Assoc. Prof. Ueda introduced me to flux growing techniques for preparing single crystals of inter-metallic compounds and we started initial experiments for evaluating appropriate process parameters for growing the inter-metallic compound $CeCu_2Mg$. Assist. Prof. Michioka introduced me to the NMR facilities at the SSPC Laboratory and we started with NMR measurements on YCo_9Si_4. I had several opportunities to join the group seminar at the SSPC Laboratory where PhD, Master and BSc students report on their research, e.g., Katsuma presented his studies on novel YbT_6Ge_6 compounds which motivated us to perform simulations of the magnetic susceptibility based on the hexagonal crystal electric field model and to have follow up discussions on this problem.

On August 5th 2016, I participated at the International Symposium "Chemical, Physical and Mathematical Foundations of Complex Phenomena" organized by the International Research Unit of Advanced Future Studies and present a talk on "Ground state instabilities of *d*- and *f*-electrons in metals and the concept of quantum criticality".

2. Research Output

2.1. General Context

Many-particle interactions among electrons in metals lead to the occurrence of extraordinary quantum phenomena associated with the particular ground states being adopted at sufficiently low temperature. This ground state formation of correlated electrons generally involves a reduction of spin and motion degrees of freedom which is continuous in some cases, e.g. the formation of paramagnetic Fermi liquid ground states in Kondo lattice systems like $CeCu_6$ and in spin-fluctuation systems like YCo_2. In other cases, correlated electrons adopt their ground state via a symmetry breaking phase transition into a macroscopic quantum state such as superconductivity or itinerant ferromagnetism. These phenomena are known for decades and substantial experimental and theoretical progress has been achieved.

Various recent discoveries of novel ground states of correlated electrons relate to systems with ground states which are unstable against certain tuning parameters such as pressure, substitutions or external magnetic fields. Most interesting are those materials where tuning brings about a continuous, symmetry breaking phase transition between two different ground states at virtually zero-temperature, which is conceived by the concept of the quantum phase transition. Already at finite temperatures, these phase transitions are preceded (and thereby indicated) by quantum fluctuations exuding into an extended phase space. As a result, exotic physical properties such as non-Fermi liquid behavior develops. In some cases, fundamentally new correlated electronic phases are formed by quantum critical correlated electron states at low temperatures, see e.g. (Steward, 2006) for a review.

2.2. Weak itinerant ferromagnetism and metamagnetism in YCo_9Si_4 and $LaCo_9Si_4$

2.2.1. *Motivation*

The observation of superconductivity appearing in the vicinity of a pressure-tuned weak ferromagnetic to paramagnetic critical point in UGe_2 (Saxena, 2000) motivated to look for materials which are close to a ferromagnetic (FM) critical point at ambient pressure. Still very few systems are available for experimental studies of itinerant 3*d* magnetism in the weakly magnetic limit (see the overviews given by Takahashi, 2013, and Brando, 2016) and in particular there are so far just very few candidate systems for studies of the itinerant ferromagnetic quantum critical point of 3*d* metals. Most promising ones were recently summarized e.g. by Sokolov *et al.* (Sokolov, 2016).

2.2.2. Status of research

One promising candidate system for itinerant ferromagnetic to paramagnetic quantum critical phenomena relates to the solid solution $LaCo_{13-x}Si_x$ which attracted our attention because of its ferromagnetism being reported to vanish near the composition $LaCo_9Si_4$ (Rao, 1994). At this specific stoichiometry, its lattice with tetragonal space group *I4/mcm* becomes compatible for adopting full translational symmetry. Our re-investigation of $LaCo_{13-x}Si_x$ in the vicinity of the stoichiometric 1-9-4 composition revealed a monotonous decrease of the Curie temperature towards $x = 4.0$ and the absence of any FM order in well annealed, well stoichiometric $LaCo_9Si_4$ (El-Hagary, 2003). Subsequent investigations comprising single crystal X-ray studies, magnetic, specific heat, and NMR measurements as well as *ab initio* electronic structure studies revealed rather exceptional features of the paramagnetic ground state of $LaCo_9Si_4$ such as a strongly exchange enhanced Pauli susceptibility and a large quasi-particle mass enhancement due to spin-fluctuations, $\lambda \sim 3.3$, an anisotropic para-magnetic susceptibility related to a small but finite Co-orbital moment revealed by NMR and, most importantly, itinerant electron metamagnetism at exceptionally low external magnetic fields of 3.5 T for field parallel to the tetragonal *c*-axis and 6 T for fields applied in *a*-axis direction (Michor, 2004).

The close vicinity to an itinerant ferromagnetic ground state instability is further indicated by the fact that the iso-structural compound YCo_9Si_4 does exhibit spontaneous weak itinerant ferromagnetism (in combination with pronounced spin-fluctuation features) even though *ab initio* electronic structure calculations revealed hardly any difference of the 3*d* band features of YCo_9Si_4 as compared to $LaCo_9Si_4$ (Michor, 2005). For both compounds, band calculations at the experimental lattice constant yield a FM ground state which, however, becomes unstable against the paramagnetic one when slightly reducing the unit cell volume in these calculations (Michor, 2004, 2005). Thus, rather subtle differences of electronic correlations in YCo_9Si_4 and $LaCo_9Si_4$ determine whether their ground states are para- or ferromagnetic. The nature of these subtle differences is not yet resolvable by *ab initio* calculations. The weak itinerant ferromagnetism of YCo_9Si_4, with $T_C \sim 23$ K and a spontaneously ordered (average) moment $\mu_s \sim 0.16$ μ_B/Co-atom, exhibits similar figures as the prototypical weak itinerant ferromagnetic material $ZrZn_2$ with $T_C \sim 28$ K (Mattias, 1958).

Another important aspect of the itinerant magnetism of YCo_9Si_4 and $LaCo_9Si_4$ are features of reduced dimensionality of their electronic structure and the existence of further iso-structural itinerant magnetic materials such as $LaCo_9Ga_4$ and $LaCo_9Ge_4$ which are currently studied at TU Wien.

2.2.3. Present studies and results

As itinerant magnetism and spin-fluctuations are at the focus of research at SSPC Laboratory we have selected YCo_9Si_4 as the first candidate material for a more detailed analysis of its spin-fluctuation features in terms of the spin-fluctuation model by Professor Takahashi (Takahashi, 1986, 1997, 2013) and for NMR studies of its ferromagnetic state as well as its spin-fluctuation physics which are currently in progress. Next to the investigation of polycrystalline YCo_9Si_4 samples we are planning to perform NMR studies on a $LaCo_9Si_4$ single crystal which was grown earlier at TU Wien. The single crystal studies of $LaCo_9Si_4$ are expected to reveal far more detailed features of the itinerant electron metamagnetic transition as compared to preceding studies on polycrystalline samples (Michor, 2004).

An initial (preliminary) analysis isothermal field dependent magnetization as well as temperature dependent magnetic susceptibility data of YCo_9Si_4 has been performed in terms of the spin-fluctuation concept by Professor Takahashi and characteristic spectral parameters T_0 and T_A characterizing the double Lorentzian distribution of the complex dynamical susceptibility $\chi''(\omega, k)$ in frequency and wave vector space have been determined. Magnetic data of YCo_9Si_4 are rather well consistent with this model yielding initial estimates of the spectral parameters $T_A \cong 1700$ K and $T_0 \cong 1200$ K, i.e., the ferromagnetic Curie temperature $T_C = 23$ K is only about 2% of the characteristic frequency width of the imaginary part of the dynamical susceptibility. These parameters T_A and T_0 in combination with T_C and the spontaneously ordered ferromagnetic moment p_s are the essential input parameters of the spin-fluctuation model and allow a variety of theoretical predictions within this concept. A simulation of the inverse paramagnetic susceptibility based on (Takahashi, 1997) and its comparison with experimental data provides us a rough estimate for the degree of reduced dimensionality which in the case of YCo_9Si_4 appears moderately close to the two dimensional limit. Of course, we are currently checking the consistency of our parameter set with NMR measurements being in progress. In parallel to the experimental work at the SSPC Laboratory, co-workers at TU Wien are performing *ab initio* electronic structure calculations for YCo_9Si_4 and $LaCo_9Si_4$ including studies of the Fermi surface topology as well as parameters such as the electric field gradients at the cobalt lattice sites which are relevant for analyzing the NMR data.

2.3. Studies of cerium and ytterbium based strongly correlated electron systems

2.3.1. *Kondo-lattice physics and geometrical frustration*
Magnetic ground state instabilities and features of quantum criticality in inter-metallic systems of cerium and ytterbium are in most cases related to competing effects of RKKY-type magnetic exchange interactions favoring a state of long range magnetic order and Kondo-type interactions supporting a paramagnetic Fermi-liquid ground state. The quantum critical point of this scenario, thus, relates to the specific situation of a mutual balance between these two competing mechanisms. In recent years, geometrical frustration has been identified as a further aspect which is relevant for cerium and ytterbium systems with specific structural features such as a triangular, honeycomb-type or Kagome-type arrangement of the magnetic ions (see e.g., Sereni, 2009).

2.3.2. Status of research on $CeCu_2Mg$
At TU Wien, in cooperation with Professor Giovannini (Genoa, Italy) and Professor Sereni (Bariloche, Argentina), we are currently investigating the compound $CeCu_2Mg$ which displays a paramagnetic ground state with various features indicating its close vicinity towards an anti-ferromagnetic instability such as a large accumulation of entropy gain a low temperatures and rather robust Ce magnetic moments (Giovannini, 2006). Specific features such as the response of various physical properties (e.g., the specific heat and electrical resistivity) to the externally applied magnetic field are, however, rather different from those of other cerium systems with a similarly close vicinity to a magnetic instability. As in $CeCu_2Mg$, adopting a hexagonal $GdPt_2Sn$ structure type, Ce ions are arranged in layers with a triangular lattice geometry, geometrical frustration is considered as a source of the observed, less common features of $CeCu_2Mg$.

2.3.3. Studies of flux-growth techniques
The present studies on $CeCu_2Mg$ are still based on polycrystalline samples which, however, impede the evaluation of important details such as the ground state wave functions of the Ce $4f^1$ state in the hexagonal crystalline electric field and the corresponding magnetic anisotropy. The latter may be easily estimated on the basis of single crystal magnetic susceptibility data. Accordingly, single crystals are highly demanded for studying the relevance of magnetic frustration and Kondo interactions with respect to the stabilization of the paramagnetic ground state of $CeCu_2Mg$ and with respect to its peculiar features. We have, thus, started to evaluate the feasibility of flux growing single crystalline $CeCu_2Mg$ at the SSPC Laboratory and we are in progress with testing appropriate flux compositions and crucible materials. A first attempt with an Al_2O_3 crucible failed due to a reaction of cerium with Al_2O_3. Next attempts will be conducted using more inert boron-nitride and tantalum crucibles.

2.3.4. Studies of novel Yb compounds
Studies of ytterbium based novel compounds and their magnetic properties have a long tradition at the SSPC Laboratory as well as at TU Wien and research on ytterbium compounds has already been subject of earlier cooperation (e.g., Tsujii, 1997a, 1997b). We, thus, have been discussing various novel ytterbium compounds presently being studied at the SSPC Laboratory and in some cases we have made attempts of modeling properties such as single crystal magnetic susceptibility and magnetic specific heat contributions by means of crystalline electric field simulations.

3. Outlook on future co-operation and interdisciplinary studies

3.1 Studies of magneto-volume effects caused by itinerant magnetism and spin-fluctuations

One of the important and contemporary aspects of itinerant magnetism are magneto-volume effects which include the magnetic contribution to the thermal expansion, the magneto-striction and the effect of externally applied pressure on the magnetic properties. Thereby, contributions of spin-fluctuations to these magneto-volume effects is still subject of on-going theoretical debates (see e.g., Takahashi, 2013). Accordingly, combined studies of magneto-volume effects and of the corresponding spin-fluctuation characteristics are highly demanded. The former has been a long-standing focus at TU Wien where a miniature capacitance dilatometer cell for thermal expansion and magneto-striction measurements has been developed (Rotter, 1998) and studies of magneto-volume effects due to itinerant magnetism and thermally induced magnetic spin-fluctuations are subject of our ongoing research at TU Wien (see e.g., Lorenzer, 2010). These investigations are further complemented by high pressure studies of itinerant ferromagnets (Maramatsu, 2008). The SSPC Laboratory with its large expertise on studies of itinerant magnetism and spin-fluctuation physics and with its very strong collaboration with a leading theoretician in this field, Professor Takahashi, is the ideal partner for a joint long term project on magneto-volume effects originating from itinerant magnetism and spin-fluctuations. Combining studies of the thermal expansion and magneto-striction with a detailed characterization of their spin-fluctuation features via NMR techniques and extending these studies to a broader range of relevant systems such as $LaCo_9Si_4$, YCo_9Si_4, and $LaCo_2P_2$ (Imai, 2015), among others, may provide an experimental base for testing current theoretical approaches on magneto-volume effects related to itinerant magnetism and spin-fluctuation physics and may possibly also provide valuable input for further refinements of theoretical approaches. The present studies on YCo_9Si_4 described in section 2.2.3. in combination with our preceding studies of its magneto-volume coupling are a first step addressing these targets.

3.2. Interdisciplinary applied research for potential use of magnetic nano-particles in medical diagnostics applications.

At TU Wien we are currently involved in a project led by the Vienna University of Life Sciences aiming to develop magnetically doped, water soluble nano-particles for the application as photo-luminescent quantum dots and simultaneously as magnetic marker substances (Zaba, 2016). These particles may ideally be detectable by magnetic resonance imaging. With the expertise on magnetic materials at TU Wien and at the SSPC Laboratory and with the special expertise of Professor Yoshimura and his group on magnetic resonance techniques we are planning to contribute some proposals to these studies which may have future relevance for medical diagnostics.

Acknowledgment

This research fellowship was financed by the International Research Unit of Advanced Future Studies at Kyoto University. I would like to express my appreciation to the Division of Chemistry for hosting me, to the International Research Unit of Advanced Future Studies for providing financial support, to Professor Yoshimura for inviting me, and to him and all members of his team for numerous interesting discussions and a very pleasant and scientifically highly productive time at the SSPC Laboratory.

Finally, I like to thank my colleague at TU Wien, Professor Reissner, for his support by accepting to take over my lecturing duties at TU Wien while being on leave to Kyoto University.

References

Brando, M, Belitz, D., Grosche, F. M. and Kirkpatrick, T. R., Metallic quantum ferromagnets. *Rev. Mod. Phys.*, **88**, 025006, 2016

El-Hagary, M., Michor, H., Wind, M., Bauer, E., Hilscher, G. and Rogl, P., Magnetic behavior of $LaCo_{13-x}Si_x$ in the vicinity of the critical concentration $x = 4$. *J. Alloys Compounds,* **367**, 239, 2003

Giovannini, M., Bauer, E., Hilscher, G., Lackner, R., Michor, H. and Saccone, A., Structure and Kondo properties of the novel compound $CeCu_2Mg$. *Physica B*, **378–380**, 831, 2006

Imai, M., Michioka, C., Ueda, H. and Yoshimura, Y., Static and dynamical magnetic properties of the itinerant ferromagnet $LaCo_2P_2$. *Phys. Rev. B* **91**, 184414, 2015

Lorenzer, K.-A., Michor, H., Müller, H. and Hilscher, G., Magnetostriction studies on the itinerant electron metamagnet $LaCo_9Si_4$. *J. Phys.: Conf. Series*, **200**, 012117, 2010

Matthias, B. T. and Bozorth, R. M., Ferromagnetism of a Zirconium-Zinc Compound, *Phys. Rev.,* **109**, 604, 1958

Michor, H., El-Hagary, M., DellaMea, M., Pieper, M. W., Reissner, M., Hilscher, G., Khmelevskyi, S., Mohn, P., Schneider, G., Giester, G. and Rogl, P., Itinerant electron metamagnetism in $LaCo_9Si_4$. *Phys. Rev. B,* **69**, *R*081404, 2004

Michor, H, El-Hagary, M, Ozcan, S, Horyn, A, Bauer, E, Reissner, M, Hilscher, G, Khmelevskyi, S, Mohn, P., Weak itinerant ferromagnetism in YCo_9Si_4. *Physica B,* **359-363**, 1177, 2005

Muramatsu, T., Tokuoka, K., Bauer, E., Michor, H., Fornasari, L., Kagayama, T. and Shimizu, K., Magnetic instability of weak ferromagnetic YCo_9Si_4 under pressure. *Physica B*, **403**, 1328, 2008

Rao, G. H., Liang, J. K., Zhang, Y. L., Cheng, X. R. and Tang, W. H., Crystal structure and magnetic properties of $LaCo_{13-x}Si_x$ compounds. *Appl. Phys. Lett.,* **64**, 1650, 1994

Rotter, M., Müller, H., Gratz, E., Doerr, M. and Loewenhaupt, M., A miniature capacitance dilatometer for thermal expansion and magnetostriction. *Rev. Sci. Instruments*, **69**, 2742, 1998

Saxena, S. S., Agarwal, P., Ahilan, K., Grosche, F. M., Hasselwimmer, R., Steiner, M. J., Pugh, E. Walker, I. R., Julian, S. R., Monthough, P., Lonzarich, G. G., Huxley, A., Sheikin, I., Braithwaite, D., Flouquet, J., Superconductivity on the border of itinerant-electron ferromagnetism in UGe_2. *Nature,* **406**, 587, 2000

Sereni, J. G., Gómez Berisso, M., Braghta, A., Schmerber, G. and Kappler, J. P., Unstable Shastry-Sutherland phase in Ce_2Pd_2Sn. *Phys. Rev. B,* **80**, 024428, 2009

Stewart, G. R., Non-Fermi-liquid behavior in d-and f-electron metals. *Rev. Mod. Phys.*, **73**, 797, 2001; Addendum *Rev. Mod. Phys.*, **78**, 743, 2006

Takahashi, Y., On the Origin of the Curie-Weiss Law of the Magnetic Susceptibility in Itinerant Electron Ferromagnetism. *J. Phys. Soc. Japan,* **55**, 3553, 1986

Takahashi, Y., Spin-fluctuation theory of quasi-two-dimensional itinerant-electron ferromagnets. *J. Phys.: Condens. Matter,* **9**, 10359, 1997

Takahashi, Y., Spin Fluctuation Theory of Itinerant Electron Magnetism. *Springer Tracts in Modern Physics,* Vol. **253**, Springer Berlin Heidelberg 2013

Tsujii, N., He, J., Yoshimura, K., Kosuge, K., Michor, H., Kreiner, K. and Hilscher, G., Heavy-fermion behavior in $YbCu_{5-x}Ag_x$. *Phys. Rev. B,* **55**, 1032, 1997a

Tsujii, N., He, J., Amita, F., Yoshimura, K., Kosuge, K., Michor, H., Hilscher, G. and Goto T., Kondo-lattice formation in cubic-phase $YbCu_5$. *Phys. Rev. B,* **56**, 8103, 1997b

Zaba, C., Part, F., Bixner, O., Grünewald, T., Michor, H., Schrittwieser, S., Hann, S., Lichtenegger, H. and Sinner E.-K., Synthesis of water-dispersible iron-doped core-shell nanocrystals – comparison between core- and shell doping. *Journal of Colloid and Interface Science*, to be submitted, 2016