Future of Emerging Novel Quantum Phases in Frustrated Magnets – an Estonian-Japanese perspective

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Abstract. This report reviews my research activities conducted while present and working as Distinguished Visiting Professor 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 key interest of my research is on emerging novel quantum phases and quantum critical phenomena in strongly frustrated quantum magnets, especially in low dimensional metal oxides and intermetallic compounds. Thereby, two classes of materials are in the focus of my present work. Firstly, studies of low-dimensional oxide materials in vicinity of magnetic field induced quantum critical points, the origin of the magnetic frustration with nearly and weakly ferromagnetic compounds, and the characterization of their spin-fluctuation features. The second focus is on cerium and ytterbium based metals with electronic ground state instabilities being related to the mechanisms of Kondo- and/or valence fluctuation effects. As a related activity, we are also working on improvements in various classes of permanent magnet materials. Finally, some future collaboration plans of the SSPC Laboratory with several of my collaborators at the National Institute of Chemical Physics and Biophysics (NICPB/KBFI) in Estonia are outlined: doped magnetism in nonmagnetic oxides, atomic layer deposition of simpler and more complex oxides and metals, development of magnetic nanoparticle agents for medical uses, targeting also interdisciplinary projects between Japan and Estonia bilaterally and with additional contributing partners.

Keywords: Strongly Correlated Electron Systems, Electronic Ground State Instabilities, BEC of Magnons, Dimer Systems, Itinerant Magnetism, Spin-fluctuations, ALD, Estonia-Japan

1. Scientific Activities

My research as visiting professor at the SSPC (Kinso) Laboratory, Department of Chemistry, Graduate School of Science, Kyoto University was conducted from April 1st to May 31th, 2019 in collaboration with Prof. Yoshimura, Assoc. Prof. Ueda, Assist. Prof. Michioka, and students in their research group (Fig. 1). During these two months, I had opportunities to discuss with Prof. Yoshimura scientific problems of quantum magnetism as well as of cerium or ytterbium based strongly correlated electron materials, both as bulk and also more applicable thin film forms. Assoc. Prof. Ueda taught me the flux growing techniques for preparing single crystals of inter-metallic compounds. Assist. Prof. Michioka introduced me to the magnetometry and NMR facilities at SSPC Laboratory. I had several opportunities to join and participate in the group seminars of SSPC Laboratory.

From May 12th until 18th I visited several other outstanding and strong laboratories in East-Japan: Tokai/J-PARC, ISSP of Tokyo University, and Tohoku University in Sendai. Both in Tokai (May 13th)

and Sendai (May 17th) I gave seminar talks on NMR studies of 2D cuprate quantum magnets. At ISSP, there I had an opportunity to conduct collaboration discussions with Prof. Kimura, Prof. Kohama, Prof. Hiroi, Prof. Takigawa, and Prof. Lippmaa. During my final weeks in Kyoto, I gave two more seminar talks. On May 23rd, I presented a seminar on our recent NMR results on 2D and 1D quantum magnets at Department of Physics, Kyoto University. On May 24th, I gave an extended seminar on the somewhat broader topic at Department of Chemistry, Kyoto University, to describe my activities over almost 25 years, since our original work with Prof. Yoshimura on Shastry-Sutherland lattice at UIUC Charlie Slichter's NMR laboratory back in 1990-ties [1]. I'm very thankful to Prof. Kenji Ishida and to Prof. Kazuyoshi Yoshimura for organising these seminars at Department of Physics and Department of Chemistry, respectively.

Figure 1. Members of the Kinso Laboratory of Kyoto University as of April 2019. 2nd row from left: Prof. Kazuyoshi Yoshimura, Hiroki Kazahaya (BC4), Prof. Raivo Stern, Shotaro Onoda (MC1), Kensuke Nara (MC1), Haruka Morishita (DC3), and Kodai Moriyama (MC2). 1st row from left: Ryoko Washino (BC4), Shigeru Imanishi (MC2), Ryochiro Matsui (BC4), Yota Okutsu (MC1), Masahiro Hayashi (BC4), Shunsuke Yamanaka (MC2), and Hajime Neo (BC4). Missing from the photo are Prof. Hiroaki Ueda and Prof. Chishiro Michioka.

2. Research Output

2.1. General Context

Many-particle interactions among electrons in metals and metal oxides lead to the occurrence of extraordinary quantum phenomena associated with particular ground states 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 or in ferromagnetic spin-fluctuation systems). 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 whose ground states are unstable with respect to certain tuning parameters such as pressure, chemical 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 (QPT). Already at finite temperatures, these phase transitions are preceded (and thereby indicated) by quantum fluctuations resulting in exotic physical properties (e.g. non-Fermi liquid behavior). In some cases fundamentally new correlated electronic phases are formed by quantum critical correlated electron states at low temperatures. In our cooperation between the Kinso Lab in Kyoto and the Lab of Chemical Physics of NICPB/KBFI in Tallinn, we discussed and located some promising materials (discussed in next section in more details) where the tuning could be done by chemical substitution or

by use of strong and ultra-strong magnetic fields. On other systems, already just the ability to grow high quality single crystals takes the research to qualitatively higher level.

2.2. Materials

I'm listing here some of the most intriguing and interested systems, we've already been collaborating on or for which we have found a common ground and platform to launch a collaborative effort. Our possible future collaborations are by no means limited to systems described in following subsections.

2.2.1. $SrCu_2(BO_3)_2$

The Shastry-Sutherland compound $SrCu_2(BO_3)_2$ [1] is not only the very first material our collaboration was started with more than 20 years ago, but arguably by now also the most studied frustrated quantum magnet. The recent NMR study [2] suggested a quite complete interpretation for all the magnetization plateaus, so called incomplete devil's staircase. They reported on NMR and torque measurements in magnetic fields up to 34 T that reveal a sequence of magnetization plateaus at 1/8, 2/15, 1/6, and 1/4 of the saturation and two incommensurate phases below and above the 1/6 plateau. We have recorded some preliminary NMR data up to the 1/3 plateau at NHMFL in Tallahassee using the He-3 fridge [3]. Most interesting perspective here is to address the reported [4,5] 2/5 and 1/2 plateaus by NMR with novel apparatus [6] developed at HLD Dresden. This requires performing pulsed NMR experiments at low temperatures in pulsed magnets up to fields beyond 74 T, and later towards 85 T. We have performed successfully the pilot NMR experiments in pulsed magnets [7], reported our results on ^{11}B-NMR line shapes up to 54 T [8], have recorded unpublished data up to 72 T fields (which should be the current record field for NMR, manuscript in preparation), and demonstrated the readiness of our NMR approach. Currently we are waiting for the next generation user magnet to become available in Dresden to take us beyond the 1/3 plateau.

There are more exciting developments on that model system – changing ground states from dimers to a 4-spin plaquette singlet state under high pressure [9] and by obsewrving emergent bound states and impurity pairs by doping/diluting the dimer network via substituting for Cu nuclei [10]. Using the high level know-how from Kinso lab in growing such high quality single crystals would open several highly promising cooperation pathways.

2.2.2. $BaCuSi_2O_6$ and $Sr_{0.1}Ba_{0.9}CuSi_2O_6$

The quasi-2D crystal structure of $BaCuSi_2O_6$ (Han purple) is shaped by an alternation of two inequivalent magnetic bilayers. Each bilayer is formed by entities comprising two magnetic CuO_4 plaquettes stacked on top of each other with a slight tilt. Within the bilayer, these entities are arranged in a square-lattice-like fashion. The neighboring bilayers are shifted with respect to each other. Since the discovery of the Bose-Einstein condensation of magnons [11], the Han purple BaCuSi2O6 is actively studied from both experimental [12-18] and theoretical [14-15, 19-21] side. The key element of the magnetic model is dimers formed by the stacked CuO_4 squares. Yet, the details of the microscopic magnetic model remain obscure. In particular, the nature of interdimer couplings that are crucially important for the condensation of magnons is controversially discussed. The perplexing behavior of pure Han purple originates from its crystal structure that changes around 100 K, so that the atomic arrangement of the room-temperature polymorph considered in earlier studies does not describe the low-temperature physics observed in the experiment. Our recent crystallographic work [22] sheds light on the actual low-temperature crystal structure and facilitates renewed microscopic insight. Below 100 K, Han purple becomes orthorhombic (space group I bam) and features two types of nonequivalent bilayers [22], denoted A and B, in agreement with more than one type of spin dimers that were observed by inelastic neutron scattering (INS) [13] and nuclear magnetic resonance (NMR) [14]. We performed low-temperature (low-T, sub-liquid-N2) high-speed high-resolution [29]Si solid-state (cryoMAS)[23] NMR studies on pure Han purple [24] confirming the presence of the A- and B-bilayers. We recently also applied state-of-the-art DFT techniques and presented a robust microscopic scenario [25] for both high-temperature tetragonal and low-temperature orthorhombic phases of pure

material. We showed that: i) the A and B bilayers indeed lead to two types of spin dimers, in perfect agreement with NMR [24, 26]; ii) the couplings between the bilayers are intrinsically non- frustrated, as they do not compete with the ordering within the dimer plane.

Recently [27], we showed that small Sr doping stabilizes the tetragonal structure in $(Ba_{1-x}Sr_x)CuSi_2O_6$, the detailed report of large crystal growth has also appeared [28]. High field NMR on single crystals of this "healed" material at EMFL/LNCMI Grenoble and torque magnetization results obtained at NHMFL Tallahassee have demonstrated clear BEC behavior around H_{c1} as expected.

2.2.3. InCuPO₅

One of the major finding of our recent work in Tallinn on a polycrystalline sample of $InCuPO_5$ is an error overlooked in the earlier report [29], due to the lesser sensitivity of the bulk magnetic probe. In our work, we confirmed using cryoMAS NMR [23] that the upturn in M vs. T measurement is intrinsic. This result might be caused due to the random singlet state formed by some spin vacancies or broken bonds within the system. To obtain a definitive conclusion, we need to perform measurements down to lower T on a high quality single crystal. Kinso Lab has the skills and experience for growing such a crystal.

2.2.4. AgVOAsO₄

Magnetic susceptibility, high-field magnetization, and electron spin resonance measurements identify $AgVOAsO_4$ as a gapped quantum magnet with a spin gap $\Delta \simeq 13$ K and a saturation field $\mu_0H_s \simeq 48.5$ T [30]. The temperature-dependent NMR shift K(T), which is a direct measure of the intrinsic spin susceptibility, agrees very well with the spin-1/2 alternating-chain model, justifying the assignment of the spin lattice. From the analysis of K(T), magnetic exchange parameters were estimated as follows: the leading exchange $J/k_B \simeq 38.4$ K and the alternation ratio $\alpha = J'/J \simeq 0.69$. The transferred hyperfine coupling between the ^{75}As nucleus and V^{4+} spins obtained by comparing the NMR shift with the bulk susceptibility amounts to $A_{hf} \simeq 3.3T\mu_B$ [31]. The unusual spin model and the low energy scale of the exchange couplings make $AgVOAsO_4$ a promising candidate for an experimental investigation of Bose-Einstein condensation in high magnetic fields [32]. All the current results have been obtained on powder samples. For high field NMR studies a single crystal is ultimately needed.

2.2.5. Bi₆V₃O₁₆

Recently, in Tallinn we have investigated the local (NMR) and bulk (magnetization and heat capacity) properties of a vanadium based S=1/2 spin chain compound $Bi_6V_3O_{16}$ ($Bi_4V_2O_{10.66}$) [33]. In the low temperature-phase, the magnetic ions (V^{4+}) are arranged in one-dimensional chains. The magnetic susceptibility shows a broad maximum around 50 K signifying a short-range magnetic order. The ^{51}V cryoMAS-NMR measurements clearly show, that the magnetic V^{4+} and non-magnetic V^{5+} species are located on different crystallographic sites with no mixed occupation. The spin susceptibility calculated from the shift of the ^{51}V NMR spectra reproduces the behavior observed in magnetic susceptibility and concurs well with the S = 1/2 uniform spin chain model with J = 113 K. Unfortunately, cryoMAS on polycrystalline samples only delivers data down to ca 20 K, for static measurement powder NMR lines are too broad. To finalize the NMR investigation of this system, a high-quality single crystal would be extremely valuable and helpful.

2.2.6. Li₂ScMo₃O₈ and Li₂InMo₃O₈

Back in 2015 Kinso lab the macroscopic and microscopic physical properties of S = 1/2 Mo_3 cluster magnets $Li_2ScMo_3O_8$ and $Li_2InMo_3O_8$ were investigated [34]. $Li_2InMo_3O_8$ shows magnetic ordering at T_N ~12 K, while no magnetic ordering is observed down to 0.5 K in $Li_2ScMo_3O_8$ in spite of the strong antiferromagnetic interaction among clusters probed by the Weiss temperature. ^{115}In and ^{45}Sc NMR measurements on static polycrystalline samples demonstrated that there should be difference in charge

fluctuation in clusters between $Li_2InMo_3O_8$ and $Li_2ScMo_3O_8$. That result suggested that the origin of different ground states realized in $Li_2InMo_3O_8$ and $Li_2ScMo_3O_8$ could be the different condition in charge and local structure as one of characteristics of the cluster magnet. We suggest to run our cryoMAS experiments on those samples in Tallinn, to resolve more detailed microscopic characteristics of their NMR behavior.

2.2.7. $TiPO_4$ and $NaTiSi_2O_6$

True inorganic spin-Peierls materials are extremely rare, but some Ti oxides can be considered to be ideal candidates owing to their well separated chains of edge-sharing TiO_6 octahedra. Back in 2011 we reported a polycrystalline $TiPO_4$ with unprecedentedly high transition temperatures of 74 and 112 K [35]. In meantime we have measured complete set of NMR data on a single crystal of $TiPO_4$. The other material, polycrystalline $NaTiSi_2O_6$ was originally reported already in 2002 [36], but has been recently reinvestigated as having an orbital-assisted Peierls ground state [37] with a single transition temperature of 210 K. There has not yet been any successful single crystal growth reported on this system, so hopefully the expertise of the Kinso lab might come handi in preparing one.

2.2.8. $YbInCu_4$

The intermetallic compound $YbInCu_4$ undergoes an iso-structural 1st - order valence-changing phase transition from a state with localized moments of the Yb into a Fermi liquid state with strong Kondo screening [38], and is known to show a gradual meta-magnetic transition in high fields over 30 T [39, 40]. Studies of ytterbium based novel compounds and their magnetic properties have a long tradition at the SSPC Laboratory and research on ytterbium compounds has already been subject of earlier cooperation. We, thus, have been discussing various ytterbium compounds presently studied at the SSPC Laboratory, especially in light of high magnetic field NMR investigations, in particular of pulsed NMR in pulsed fields and low temperatures [8].

2.2.9. $La_xBa_{1-x}Fe_{12-y}Co_yO_{19}$

The hexaferrite systems remain a perspective path for permanent magnets, especially in light of collapsing availability of rare-earth metals like Nd and Dy. Systematic investigation of the magnetic properties of La- and Co- substituted hexagonal magnetoplumbite-type (M-type) Sr-ferrite $SrFe_{12}O_{19}$ using single crystals [41] has demonstrated increase of both their saturation moments and magneto-crystalline anisotropy with doping. To specify preferential occupation sites of Co substituents and to clarify charge and spin states of Co ions in (La, Co)-co substituted $Sr_{1-x}La_xFe_{12-y}Co_yO_{19}$ (x, y <= 0.4), ^{57}Fe and ^{59}Co NMR spectra are measured under zero and external magnetic fields using powdered and single crystalline specimens [42]. The Kinso lab has grown single crystals of non-substituted M-, X-, and W-type Sr-hexaferrites by utilizing the traveling solvent floating zone technique and investigated their magnetic and electrical properties [43]. In Tallinn, we have worked on Ba-hexaferrite nanoparticles [41], and worked on U- [44] and Y-type [45] hexaferrites. Cooperation with an ultimate goal to find best ferrite magnets is well prepared on both sides.

2.2.10. $Nd_{2-x}Y_xFe_{14-y}Co_yB$

The best permanent magnets suffer increasingly from decreasing resources of rare-earth metals. We have cooperated with colleagues from Lappenranta University to gain detailed understanding of hysteresis losses first in NdFeB [46], then in all the popular permanent magnets [47] and finally in ferrite [48-51] magnets. An effort towards better micro- and nanostructure and profitable chemical substitutions in NdFeB permanent magnets could eventually speed up our progress towards electrical and magnetic motors based on sustainable permanent magnets.

3. Outlook on future co-operation and interdisciplinary studies

3.1 Studies of dopant and oxygen vacancy induced magnetic effects in non-magnetic oxides

One of the important and contemporary aspects of itinerant magnetism is emergence of magnetism by oxygen vacancies or transition metal dopants in non-magnetic oxides. We have investigated magnetic properties of Mn-stabilized cubic zirconia (ZrO_2) powder samples to verify the recent theoretical predictions [52] of ferromagnetism in transition-metal-doped ZrO_2. We found that 5% Mn-doped cubic ZrO_2 samples, when heat-treated in argon and air environments, exhibit tiny hysteresis loops at room temperature [53]. Room-temperature ferromagnetism was preserved in Ca and Mg stabilized cubic ZrO_2 in both bulk samples and in thin films prepared by pulsed laser deposition [54]. Ferromagnetism was also found in rare earth doped cerium oxide bulk samples [55]. Magnetic and structural studies and their dependence from doping in LaMnO3 thin films prepared by atomic layer deposition [56] and bulk samples prepared by citrate combustion process [57] were also reported. Expansion of those investigation to well chosen single crystal samples could add important insight to this pool of questions.

3.2 Closer to applications – studies of composite materials in form of thin films by atomic layer deposition (ALD)

For about last 10 years the magnetism group at NICPB has been collaborating with Tartu University (and more recently with Helsinki University) to develop technology of growing magnetic films and nano-composites using the atomic layer deposition (ALD) thin film growth. Various simpler and more complex systems have been explored: cobalt doped titanium oxide thin films [58], ferromagnetic iron oxide films on three-dimensional substrates with tin oxide nanoparticles [59], iron oxide and iron-magnesium oxide thin films [60], holmium and titanium oxide nanolaminates [61], holmium titanium oxide thin films [62], dysprosium oxide and dysprosium-oxide-doped titanium oxide thin films [63], bismuth iron oxide thin films of alternating bismuth oxide and iron oxide layers [64], iron erbium oxide thin films [65]. We have grown ZrO_2 [66], ZrO_2-Fe_2O_3 [67], ZrO_2-HfO_2 [68], ZrO_2 and cobalt ferrite layered nano-composite [69], and cobalt oxide and zirconium oxide nanolaminates [70]. As-synthesized magnetic Ni particles [71] as well as quasi-cubic α-Fe_2O_3 nanoparticles [72] have been embedded in ALD TiO_2 thin films. Finally, the Intermetallic Co_3Sn_2 and Ni_3Sn_2 [73] as well as nonmagnetic Ni_3N and magnetic Ni metal [74] thin films have been grown by ALD. Such a massive expertise in ALD growth can be employed to create thin film versions of several excellent single crystal compounds created at the Kinso laboratory.

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

At NICPB we are currently involved in a project aiming to develop magnetically doped nano-particles to be incorporated as magnetic marker substance that may ideally be detectable by magnetic resonance imaging [71, 72]. With the expertise on magnetic materials at the SSPC Laboratory of Prof. Yoshimura and his group and the special expertise on magnetic resonance techniques at Tallinn we are planning to contribute some proposals to these studies that may have future relevance for therapy and/or medical diagnostics.

4. Acknowledgment

5. References

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