

ICC-IMR FY2015 Activity Report

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ICC-IMR FY2015 Activity Report

International Collaboration Center

Institute for Materials Research Tohoku University

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Mission

The ICC-IMR was founded in April 2008 as the center for international collaboration of the Institute for Materials Research (IMR) a center of excellence in material science, consisting of 27 research groups and five research centers. The ICC-IMR works as a gateway of diverse collaborations between overseas and IMR researchers. The ICC-IMR has invited 45 visiting professors and conducted 19 international research projects since its start-up (please inspect the graph below for more details,). The applications are open to foreign researchers and the projects are evaluated by a peer-review process involving international reviewers.

ICC-IMR coordinates six different programs:

- 1) International Integrated Project Research
- 2) Visiting Professorships
- 3) Short Single Research Visits
- 4) International Workshops
- 5) Fellowship for Young Researcher and PhD Student
- 6) Material Transfer Program

We welcome applicants from around the globe to submit proposals! Visitors supported by ICC-Programs



USA	74
China	57
Germany	51
Korea	43
France	39
UK	32
Netherlands	17
Russia	15
India	- 8
Switzerland	- 7
Iran	6
Canada	- 6

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Czech Republic 2
Thailand 2
Argentina 1
Austria 1
Belgium 1
Indonesia 1
Rumania 1
Slovakia 1
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Activity Report

Visiting Scholars



Visiting Scholars

FY 2015 Visiting Scholars

	No.	Candidate	Host	Proposed Research	Title	Affiliation	Term
15	15G1	Petre Badica	K. Watanabe	Joints of Superconducting Tapes: Fabrication and Characterization	1st degree Senior Researcher	National Institute of Materials Physics, Romania	2015.5.1-6.4
15G2Jens MüllerT. SasakiInvestigation of Low Charge and Spin Dy Correlated □-Electro Multi-Degrees of Free		Investigation of Low-Frequency Charge and Spin Dynamics in Correlated □-Electron Systems with Multi-Degrees of Freedom	Professor	Institute of Physics, Goethe-University Frankfurt, Germany	2015.9.17-12.15		
15G3	15G3	Victor Nemykin	R. Belosludov	Theoretical Investigation of the Electronic Structure and Spectroscopy of Organometallic and Transition-metal Nanostructures	Professor	University of Minnesota Duluth, USA	2015.6.23-7.26
15G4	Pallavi Dhagat	K.Takanashi	Characterizing Magnetostriction in FeFtPd Thin Films	Associate Professor	Oregon State University, USA	2015.6.23-7.22	
	15G5	Lech Baczewski	K. Takanashi	Structural and Magnetic Studies on L1 ₀ -type FeNi Ordered Alloys	Professor, Head of Laboratory	Institute of Physics Polish Academy of Sciences, Poland	2015.11.9-12.8

Superconducting Y-123 joints by Spark Plasma Sintering

Abstract: Spark Plasma Sintering (SPS) was applied for fabrication of superconducting joints. Joints were realized between stacked two Y(Gd)Ba₂Cu₃O₇ commercial tapes, tape-bulk-tape or bulk-bulk where the bulk from the middle of the stack was of ErBa₂Cu₃O₇. Some of the arrangements and for some processing conditions joints have shown zero resistance below 35K.

To realize persistent magnetic coils generating high magnetic fields, use of superconductors is required. Coated tapes of high temperature superconductor REBa₂Cu₃O₇ (123, RE-rare earth elements) are at present suitable candidates delivering high performance at acceptable prices. Their application requires fabrication of superconducting joints [1, 2]. In this work we explored the possibility to use spark plasma sintering (SPS) for the fabrication of joints. Spark plasma sintering is a method that applies a pulsed current on the punches of a mold (usually from graphite as in this work) loaded with the samples to be sintered. Simultaneously on the punches a uniaxial pressure is also applied. The method is flexible ensuring high heating and cooling rates.

Table 1. Samples (S), arrangement, SPS conditions, post-annealing conditions, zero-resistance critical temperature (Tc0).

S	Etching (time,	arrangement	SPS	Post-	Tc0 (K),
	H2O2/HNO3)		conditions	annealing	observations
Raw	-	-	-	-	92.45
tape					
Α	40s, 2.4/1	-	-	-	92.55
В	100s, 1/2.4	-	-	-	89.45
С	60s, 2.4/1		-	-	Sharp transition
		h-BN	Pressed at		above 93.45K, it has
			20°C at 18KN		residual resistance
		Ag			
D	-		400°C/3min/	-	Multiple transitions,
			18KN		it has residual
			-		resistance
E	60s, 2.4/1		300°C/3min/	-	Multiple transitions,
		h-BN	18KN		above 35.5K
		A			
		Ag			
F	-	Y123	870°C/3min/	470°C/60	Multiple transitions,
			15KN	h/O ₂	above 35K
		Er123			
		Y123			
G	60s, 2.4/1		870°C/3min or	470°C/60	Resistance
	,		850°C/3min/	h/Q2	measurement in
		En122	15KN	11.02	progress
		Er123	1.71218		ProBross

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In our experiments we used different arrangements as follows: bulk-bulk-bulk, tapebulk-tape and tape-tape (Table 1). Commercial tapes were of Y(Gd)Ba₂Cu₃O₇. The outer bulks of the sandwich-like stacks were of YBa₂Cu₃O₇, while the middle ones were of ErBa₂Cu₃O₇. Bulks were obtained in the lab. by the solidstate-reaction.

As SPS sintering media hexagonal BN powder was used. The SPS atmosphere was of Ar (0.75 atm). Other processing conditions including post-annealing in oxygen are presented in Table 1.

During preliminary experiments it was found that etching conditions for Ag removal from the surface of the superconducting layer of the tape can influence the quality of the tape (compare samples raw tape, A and B in Table 1 and Fig. 1). It was also found that Ag-cover is useful for a better mechanical strength of the joint.

SPA processing temperatures were from 300 up to 890°C. Pressing at room temperature or heating by SPS at low processing temperatures of 300, 400°C (samples C-E in Table 1, Fig. 1) indicated that joints formed, but they are not metallurgical and, hence, they are not mechanically stable and the reproducibility is low. Samples (e.g. F, Table 1, Fig. 1) fabricated at high temperatures attain zero resistance after post-annealing treatments to introduce oxygen depleted during SPS processing. In such a case, zero resistance was measured below 35K and a metallurgical joint

was realized. Therefore, a high SPS-processing temperature (around 830-870°C) followed by post-annealing in oxygen is required and optimization process (sample G, Table 1, Fig. 1) is in progress. Optimization of the pressing pressure during SPS and of annealing conditions is also under investigation.

In summary, presented results are promising and it is of interest to further explore application of SPS for fabrication of superconducting joints.

References

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Fig. 1 Reduced resistance versus temperature curves. Sample notation is as in Table 1.

Keywords: joining, sintering, annealing, superconducting Petre Badica (National Institute of Materials Physics, Romania) E-mail: <u>badica2003@yahoo.com</u>

Investigation of Low-Frequency Charge- and Spin-Dynamics in Correlated π -Electron Systems with Multi-Degrees of Freedom

We have investigated the dynamics of correlated charge carriers in the square-lattice dimer Mott insulator β '-(BEDT-TTF)₂ICl₂ by means of low-frequency fluctuation spectroscopy. The conductance noise power spectral density increases by seven orders of magnitude from room temperature to 70 K, the lowest temperature of our measurements, and can be described by localized fluctuations in a resistor network with variable range hopping. In a characteristic temperature region of 110 – 140 K a crossover of different transport and fluctuation regimes is observed. The localization of carriers at these temperatures is accompanied by the formation of polar nanoclusters and a slowing down of the fluctuation dynamics. From the break-up of the 1/f-type noise spectra into Lorentzian constituents which exhibit a peculiar temperature and electric field dependence we deduce the energy of the two-level fluctuation processes and a cluster size of nanopolar regions of about 20 nm.

Intradimer charge degrees of freedom in recent years have been recognized as key to understand the wealth of exotic ground states in correlated π -electron systems, as e.g. chargeorder, ferroelectric order (the combination of which may provide a new mechanism for multiferroicity recently observed in organic chargetransfer salts [1]), magnetism and superconductivity. In particular, their role for the often anomalous dielectric response of different materials/samples exhibiting short-range relaxor-type and/or long-range order currently is a matter of considerable interest.

In order to better understand the role of charge fluctuations for the observed frequency dependent dielectric properties, we designed experiments aiming to study the low-frequency charge carrier dynamics by measuring the conductance noise power spectral density of β' -(BEDT-TTF)₂ICl₂, a typical square-lattice dimer Mott system, which is a model system for testing charge fluctuations on the dimer and may serve as a reference material for the triangular lattice spin-liquid candidate κ -(BEDT-TTF)₂Cu₂(CN)₃. The technique of measuring the conductance noise power spectral density (PSD) S_G , where G = I/V is the conductance, has been developed and tested in the framework of a previous exchange of students between IMR, Sendai, and Goethe-University Frankfurt.

β'-(BEDT-TTF)₂ICl₂ orders antiferromagnetically at T_N = 22 K. The temperature dependence of the dielectric constant ε(*T*,ω) shows a peak structure obeying a Curie-Weiss law with a strong frequency dependence and a Curie temperature T_C = 67 K. The anisotropic ferroelectricity is found to be glassy in nature and the electrical dipoles are suggested to stem from charge disproportionation within the dimer [2,3].

Figure 1 shows the temperature dependence of the magnitude (main panel) and frequency exponent (inset) of the normalized conductance noise power spectral density (PSD) $S_I/I^2 \sim 1/f^{\alpha}$ taken at f = 1 Hz. The overall behavior resem-

bles that of the resistance which reaches high values of order 10 G Ω at T ~ 70 K due to the Mott gap. The fluctuations, however, increase even more strongly and reveal additional information [4,5]. The strong increase of S_I / I^2 of seven orders of magnitude upon decreasing temperature from room temperature to 70 K of magnitude is well described by an exponential increase

$$\ln(S_{I}/I^{2}) = \text{const. x} (T_{0}/T)^{2},$$

where T_0 marks the crossover from nearest neighbor hopping to variable range hopping (VRH) [6]. In this model, the strong lowfrequency dynamics is caused by localized slow fluctuations of the Coulomb potential, which modulates the conductance of nearby elements



in the resistor network. Fig.1 Conductance noise PSD of β '-(BEDT-TTF)₂ICl₂ measured in the low (blue) and high-current (red) limit. Inset shows the frequency exponent $\langle (T) \text{ from } S_1/l^2 \sim 1/f^{\alpha}$.

The frequency exponent $\alpha(T)$ shown in the inset if Fig. 1 shows a step-like increase below about 130 K from values of $\alpha \sim 0.8$ to $\alpha \sim 1$ or larger corresponding to a shift of spectral weight to low frequencies and a slowing down of the charge

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fluctuations.

In the temperature region between 110 K - 140 K the resistivity starts to strongly increase and the conductance noise PSD exhibits a change in the scaling exponent ξ in $S_G / G^2 \sim G^{\xi}$ (not shown). In the same temperature range 110 K <T < 140 K, we consistently have observed Lorentzian noise spectra superimposed on a 1/flike background and were able to fit the spectra accordingly, see Fig 2. Strikingly, as shown in Fig. 2 exemplarily for T = 123 K, above a threshold electric field *E* applied to the sample, the Lorentzian contribution becomes suppressed and its corner frequency f_c shifts to higher frequencies, while the $1/f \alpha$ background also becomes suppressed (shown in Fig. 1). We suggest that in this crossover region where pronounced two-level fluctuations are observed, switching entities, i.e. nano polar regions (NPR) that couple to the external electric field, are formed. The corner frequencies f_c at small currents, i.e. below the threshold electric field, can be described by a thermally activated behavior yielding an activation energy of about E_a = 2800 K, which is comparable to the intradimer transfer energy. However, a Vogel-Fulcher fit to the data $f_c(T)$ works equally well and yields a Vogel-Fulcher temperature of T_{VF} = 32 K, not far from the charge freezing temperature T_{VF} determined from the frequencydependent peak in the dielectric function [2]. The electric-field dependence f_c (*E*) above the threshold can be fitted by

$f_c = f_0 \ge \exp[-(E_a + pE) / k_B T]$

from which we were able to estimate the total dipolar moment p. With the local moment on the dimer of 0.13*ed* [2] a nanoscale cluster (NPR embedded in a paraelectric matrix) size of radius \sim 20 nm is estimated.

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Fig. 2 Left: Lorentzian spectra at T = 123 K superimposed on a $1/f^{\ background}$ for different currents. Solid line is the corresponding fit to the data (exemplarily shown for one curve). Right: Corner frequency f_c for different electric fields.

Keywords: electrical properties, metal-insulator transition

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Investigation of the Electronic Structure and Spectroscopy of Organometallic and Transition-metal Nanostructures

The realization of the nanomaterials with specific topology and supramolecular architecture useful for high-performance nanoscale devices is currently one of the main challenges in nanotechnology. Here we highlight our recent research activities on inorganic/organometallic functional materials for molecular electronics, light harvesting and photocatalysis.

Covalent and non-covalent donoracceptor (D-A) assemblies were intensively studied during the last several decades due to their potential use in solar energy to electricity conversion. In order to archive the high efficient solar energy conversion, the formation and stability of the long-living charge-separation state, which can be controlled by the electronic structure, type of the linking group, and geometric orientation of the light-harvesting donor and electron acceptor, is required. The D-A assemblies with covalent bonds can be controlled by the nature of the linking group. However, the preparation often requires several additional synthetic steps, which make such structures less attractive for applications. An alternative industrial approach is the formation of well-organized non-covalent assemblies, which can be controlled by dispersion interactions.

We have prepared the non-covalent complexes formed between C₆₀ and C₇₀ fullerenes substituted and boron subphthalocyanines (Fig. 1a) and examined the tunability of the subphthalocyanine core toward finding a stronger binding fullerene receptor, which improve photovoltaic heterojunctions characteristics of by electron-transfer facilitating the from subphthalocyanine to fullerene [1]. It has been found that the hexathiophenolcontaining receptor shows the largest interaction energy with fullerenes that confirmed by UV-vis data (Fig. 1b) and extensive DFT calculations (Fig. 1c).



Fig.1: Non-covalent complex formation in subphthalocyanine/fullerene system.

These systems were though as a low-cost alternative to the traditional organic light-harvesting modules for organic photovoltaics.

New trinuclear Fe-Ru-Fe tetraphenylporphyrin complexes axially coordinated with various ferrocene-based ligands, were prepared and characterized [2]. It was observed that the first oxidation process was attributed to the reversible oxidation of the Ru^{II} center, which is important for their application as molecular wires (see Fig. 2). DFT and time-dependent DFT calculations aided in correlating the spectroscopic and redox properties of studied complexes with their electronic structures.



Fig.2: Trinuclear porphyrin/ferrocene complexes [2].

organic-inorganic New spherical ferrocene-tin hydroxide clusters of general formula [(FcSn)12O14(OH)6]X2 were prepared and analysed [3]. DFT and TDDFT calculations suggest that the organometallic substituents in the [(FcSn)12O14(OH)6]²⁺ core are rather isolated from each other, and thus such a cluster can be potentially used as an electron reservoir, which can provide up to 12 electrons toward chemical processes.

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Visiting Scholars

Characterizing Magnetostriction in FePtPd Thin Films

Abstract: This collaborative work focuses on magnetostriction properties in L1₀ ordered Fe₅₀Pt_(50-x)Pd_x thin films of varying Pd content, x. In our earlier collaboration, the range of film compositions prepared was limited but suggested that magnetostriction was composition dependent and could hence be tailored by controlling the film composition. Accordingly, additional samples were sputter-deposited and their magnetostriction properties were characterized via the cantilever bending technique. Simultaneously, the crystalline structure and the magnetic anisotropy were verified by X-ray diffraction and SQUID magnetometry, respectively. Measurements and analyses are ongoing and expected to yield a deeper insight to the composition dependence of magnetostriction in these films.

FePtPd alloy films, with strong perpendicular magnetic anisotropy, are leading candidates for recording media in next-generation hard disk drives and solid state multiferroic random access memory technologies. The magnetostrictive properties of such materials are of importance, as strain can be used to manipulate their magnetic anisotropy and therefore their magnetic switching characteristics. It is known that the perpendicular anisotropy of L10 ordered FePtPd alloys increases as the Pt content is increased. Our research goal is to identify if magnetostriction follows a similar trend or maximum at intermediate has α composition.

The 100 nm thick Fe₅₀Pt_(50-x)Pd_x films were deposited directly on 0.3 mm thick sinale crystal MaO (100) substrates. The films were prepared by co-sputtering from three independent targets. The sputtering input power to the Pd and Pt targets was adjusted to obtain films with a desired Pd content, x, spanning from 0 to 50 atomic percent. FePt (x=0) and FePd (x=50) samples were also at substrate different deposited temperatures to examine the effect of temperature-driven the ordering on anisotropy and magnetostriction. Llo ordering was confirmed by X-ray diffraction measurements.

The in-plane and out-of-plane hysteresis loops of the samples were measured by SQUID magnetometry to confirm the desired strong perpendicular magnetic anisotropy.

The magnetostriction of the samples was determined using the cantilever bending method implemented on the physical properties measurement system (PPMS) available at IMR, Tohoku University, using a custom substrate clamping fixture, displacement sensor and control software. An in-plane magnetic field varying from -9 T to 9 T and back was applied along the cantilevered MgO substrate (with the FePtPd film on the bottom surface) and the deflection of the free end of the cantilever, resulting from the expansion or contraction of the film via the magnetostrictive effect, measured. The displacement as a function of the magnetic field is shown in Fig. 1 and



Fig. 1 Illustration of the cantilever bending method for magnetostriction measurement and resulting cantilever displacements plotted as a function of the applied field for samples of different Pd content, x.

to determine can be used the magnetostriction. As can be seen from these example data, there is hysteresis (due to misalignment of field direction with respect to sample plane) and sometimes lack of a significant saturation (flat) region, which has impaired conclusive analysis of these measurements. We are anticipating delivery of a 14 T PPMS at Oregon State University in September 2016; and expect to continue the measurements towards the completion of this study.

We plan a publication [1] upon the acquisition of conclusive results.

References

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Keywords: L1₀-FePt, magnetic properties, mechanical properties Pallavi Dhagat (Oregon State University) E-mail: dhagat@eecs.oregonstate.edu http://oregonstate.edu/engr/magnetics/

Ultrathin magnetic films with high perpendicular anisotropy for applications in magnetic recording

wo iron based thin films systems were studied: FeNi and FePt. Both systems are interesting in view of possible practical applications in perpendicular magnetic recording. FeNi thin films were grown by sputtering method in IMR on MgO(100) monocrystalline substrate and Fe/Pt multilayers were prepared by MBE on sapphire substrates in IPPAS in Warsaw. In both systems studied the aim is to obtain the ordered phase L1₀ with high perpendicular anisotropy. Sputtered FeNi thin films were deposited directly on MgO substrate without any buffer layer to avoid any interdiffusion during post growth annealing by RTA method. Fe/Pt multilayers were ion irradiated with different energies and doses in order to create L1₀ phase.

The aim of the study within the scientific collaboration between IMR and IPPAS is to obtain metallic magnetic thin films with high perpendicular magnetic anisotropy for application in magnetic recording. Two iron based thin films systems were studied: FeNi and FePt. I was collaborating with prof. M. Mizuguchi on FeNi and with prof. T. Seki on Fe/Pt system in the prof. K. Takanashi Magnetic Materials Laboratory at IMR.

FeNi thin films were grown by sputtering MgO(100) method at IMR on monocrystalline substrate and Fe/Pt multilayers were prepared by MBE on sapphire (0001) substrates at IPPAS in Warsaw. Sputtered FeNi thin films were deposited directly on MgO substrate without any buffer layer to avoid any interdiffusion during post growth annealing at 300 C by RTA method and in order to have a simple, not costly as MBE and easy method of growing of L1₀ FeNi phase. The long-range chemical order parameter (S) was precisely estimated by grazing incidence X-ray diffraction (GI-XRD) using synchrotron radiation at SPring-8 in the Japan Synchrotron Radiation Research Institute. S parameter was estimated from the intensity ratio between a superlattice (110) peak and fundamental (220) peak seen on the diffraction pattern. However the highest value of S of about 0.3 was obtained what is significantly lower than for MBE grown films on a relevant buffer layers[1,2]. Another type of substrates such as spinel and SrTiO3 with smaller misfit values were tried but with no success - lower S values were found or no superlattice (110) peaks were observed. For now the reason for such behavior is not clear. In the next stage of the study based on theoretical predictions, the addition of 2-5 % of Ti and V replacing Ni in the multilayered for MBE sample with large Ku constant and

structure was tried. Vanadium addition didi not help at all the formation of L1₀ FePt alloy phase and Ti addition helped but only in a limited way. Further studies and experiments are in progress. Ferromagnetic resonance Modulated FMR and Strain SMFMR experiments were performed on sputtered and MBE FeNi multilayered samples. From SMFMR magnetostriction values were obtained and λs differ from 1.97 to 5.2 x10⁻⁶ depending on the sample heat treatment. FMR measurements revealed peculiar in plane symmetry -two-fold four-fold and even six- fold depending on the preparation method.



Figure 1. Angular in-plane dependence of the resonance field measured by ferromagnetic resonance (FMR).

In Fig.1 some examples of the sin-plane symmetry are presented. Fig 1A is for sputtered sample annealed by RTA, Fig 1B is Fig 1C is for MBE sample with middle Ku

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constant.

Angular L-MOKE experiments were performed in order to compare with FMR results and also domain structure was measured as a function of magnetic field amplitude. The results need to be analyzed now and compared with X-ray in plane diffraction experiments to be performed on the same samples at Spring 8 synchrotron.

It is clear that a formation of L1₀ ordered phase of FeNi alloy is quite complicated and not so easy so more work and effort is still needed.

Another collaboration axis was established – it concerns a study of structural and magnetic properties of Heusler alloys: CFMS and CFGG type. SMFMR and FMR experiments are planned in collaboration with prof Seki and his phD student T. Yamamoto.

Changes of magnetic properties of irradiated Fe/Pt multilayers were studied in order to verify a possibility of L1₀ structure formation in the intermixed regions. Six series of Fe/Pt multilayers of different bilayer thickness and total number of bilayers were grown MBE and using subsequently irradiated with Ne+ ions of different energies and doses evaluated a priori with TRIDYN simulations. RHEED, LEED and STM in-situ measurements revealed epitaxial growth and good quality of interfaces. All as grown multilayers showed in-plane magnetization easy axis as revealed by VSM M(H) measurements. Full switching of magnetization easy axis from in-plane to out-of-plane direction was not achieved after ion irradiation but certain amount of perpendicularly magnetized phase appeared in most of irradiated samples.

The Fe/Pt samples irradiated with Ne ions of 15 keV energy and different doses (1x10¹⁵ to 5 x 10¹⁶) were annealed using RTA method at different temperatures. Next polar micro-MOKE measurements were performed in order to observe an evolution of hysteresis loops. Increase of remanence and coercive field was noted but a complete reorientation into out of plane direction was not achieved probably due to high shape anisotropy of $2\pi M_s$ and also due to (111) growth direction where the easy axis is tilted 35 deg to the sample plane. Further studies are planned – growth on MgO (100) to have (001) growth direction of ordered phase and use of different cover layer instead of Pt It was revealed that intermixing with Pt overlayer causes a formation of Pt₃Fe phase beside ordered L1₀ FePt one. New Fe/Pt multilayers of identical composition were grown by MBE and irradiated by Ne ions at elevated temperatures form 150 to 350 C in order to combine the effects of ion irradiation and temperature annealing.

Longitudinal and polar MOKE experiments were performed and they revealed oscillatory behavior of coercivity depending on ion dose and irradiation temperature. Structural analysis is in progress to explain the observed effect.

Common publication is in preparation on Fe/Pt results.

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Keywords: thin films, magnetic properties, sputtering, nanostructures, perpendicular anisotropy

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Activity Report

Workshops

FY 2015 Workshops

No.	Chairperson	Title of Workshop	Place	Date
15WS1	T. Goto	The 10th International Workshop on Biomaterials in Interface Science (Innovative Research for Biosis-Abiosis Intelligent Interface Summer Seminar 2015)	Zao, Miyagi	2015.8.4-5
15WS2	S. Orimo	10th International Symposium "Hydrogen & Energy"	Zao, Miyagi	2016.2.21-26
15WS3	A. Yoshikawa	JSPS 161/186 Committee and ICC-IMR International Joint Workshop – Crystals and Their Applications into Radiation Devices–	Sakura Hall, Tohoku University	2016.1.7-8
15WS4	M. Mizuguchi	Spin Energy Materials	House of Creativity, Tohoku University	2015.12.3-4

The 10th Anniversary International Workshop on Biomaterials in Interface Science

- Innovative Research for Biosis-Abiosis Intelligent Interface Summer Seminar 2015 -

Biosis-abiosis intelligent interface science is a new concept to develop materials and systems between human constituents and biomaterials because of strong demands for replacing various parts in human-body with artificial products. Forefront researchers and students from various fields related to biomaterials gathered at the 10th Anniversary International Workshop on Biomaterials in Interface Science on Aug. 4–5th at Sendai, Japan. The Invited lectures by five experts from abroad and 22 papers provided valuable opportunity for cross-over discussion, interdisciplinary idea sharing and new collaboration to develop and establish the intelligent interface science on biomaterials.

To meet a variety of requirements for multi-functionality under complex circumstances in human bodies, it is quite difficult by using and developing monolithic homogeneous materials. and Interdisciplinary and international activities are necessary to develop the biomaterials, such as artificial bone and tooth, and the **biomaterials** should be controlled regarding biofunctionalities and mechanical properties in a wide scales from nano- to micro-scale, as well as compatibility with human body. Three Institute in Tohoku University, namely Institute for Materials Graduate (IMR), School Research of Graduate School Dentistry and of Biomedical have Engineering, been collaborating and involved in the 5-year project on Biomaterials to establish a new concept, Biosis-Abiosis Intelligent Interface Science. As the series of international forums in the frame this project, the 10th Anniversary International Workshop on Biomaterials in Interface Science in conjunction with Innovative Research for **Biosis-Abiosis** Intelligent Interface Summer Seminar 2015 was held on Aug. 4th-5th, 2015, at Miyagi Zao, Sendai.

The 2-days technical program in this workshop included 27 papers in which 5 invited lectures were given by distinguished professors and experts on biomaterials from Australia, Thailand and China. 72 participants of professors, researchers and students attended in the workshop. Prof. Peck Christopher Charles who is the dean of Faculty of Dentistry, the University of Sydney provided an invited lecture involving the current activities of dental bioengineering in Sydney. The invited lecture by Prof. Prasit dual-leached Pavasant was on polycaprolactone porous scaffolds for bone tissue regeneration. Prof. Jukka Pekka

Keywords: biomedical, ceramic, metal Takashi GOTO (Multi-Functional Materials Science) E-mail: goto@imr.tohoku.ac.jp http://interface2015.imr.tohoku.ac.jp/

Matinlinna gave a lecture on applications of silicon chemistry in dentistry. The state-of-the-art research on biocompatibility of dental materials was provided by Dr. Jian-min Han. Dr. Alfred C. H. Yu gave an invited lecture on Understanding the interfacial biophysics in sonoporation. particularly on actin disruption and membrane blebbing. Prior to these invited lectures, Prof. Keiichi Sasaki who is the dean of Tohoku University Graduate School of Dentistry and the project leader of the collaborating 5-year project introduced the progress and present state of the project. Furthermore, presentations by speakers with various academic backgrounds provided presentations on updated research from a fields dentistry, various such as bioengineering and bio materials. These invited lectures and oral presentations gave the all participants a valuable opportunity for sharing interdisciplinary viewpoints and ideas. These collaborative discussion had great contributions to the development on the intelligent interface science on biomaterials.



Fig. 1 Group photo and shots in lectures.

Workshops

10th International Symposium "Hydrogen & Energy"

Hydrogen and metal hydrides are of key importance in designing next-generation energy storage and conversion technologies. Approximately 60 researchers ranging from students to world leading experts in the field of hydrogen energy participated in the 10th International Symposium "Hydrogen & Energy" held in Miyagi Zao, Sendai on February 21–26, and discussed their latest experimental/theoretical results.

The development of next-generation energy storage and conversion technologies utilizing hydrides is expected to play a key role in the establishment of a sustainable energy society. The 10th International Symposium "Hydrogen & Energy" serves as an information platform of the fundamental science and technology, and the frontiers of research on hydrogen and energy. The symposium was cooperatively supported by E-IMR, WPI-AIMR, and JSPS KAKENHI (S).

The symposium consisted of invited keynote lectures reviewing the key elements of the hydrogen cycle, i.e. the hydrogen production, hydrogen storage and hydrogen combustion and fuel cells. Furthermore, the conversion technologies of renewable energy in general and novel energy carriers besides and beyond hydrogen were discussed. The world leading experts presented their current research challenges and most important results in invited and contributing talks. Early stage and experienced researchers presented their latest results and the open questions on poster presentations.

This symposium provided an excellent opportunity for researchers to share their latest ideas and findings, and forge new partnerships. It was enthusiastically received by many of the participants. We would like to thank all those who involved in this symposium and support from ICC-IMR.



Fig. 1 Scenes of oral and poster sessions.



Fig. 2 Group photo.

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Report on the JSPS 161/186 committee and ICC-IMR international joint workshop -crystals and their applications into radiation devices-

JSPS 161/186 committee and ICC-IMR international joint workshop were held on 7-8th Jan. 2016 in Tohoku University. The focus of the event was fabrication of scintillation materials and their applications. The participants were 80 persons from 4 countries who research in several fields such as material science, radiation physics in academic or industrial fields.

Joint workshop -crystals and their applications in radiation devices- was held on 7-8th Jan. 2016 in Tohoku University. This workshop is organized by Japan Society for the Promotion of Science (JSPS)'s University-Industry and Cooperative Research 161st and 186th Committees and the ICC-IMR. The subjects of the JSPS 161st and 186th committees are the "Science and Technology of Crystal Growth" and "Radiation Science and Its Applications", respectively. These committees consist of over 60 academic persons and 60 companies; their research fields spread over basic science (e.g. optical physics, radiation physics), materials (crystal/ceramics growth), radiation detectors for medical imaging, nuclear power plant, etc.

Purpose of this workshop was to share the latest results among academia and industry side and to get new initiative for the innovation in several fields such as crystal companies, equipment manufacturers and researchers. Here, scintillation crystals are used in radiation detectors in several fields such as medical imaging and dose monitoring, so this topic is related to both the JSPS committees. Thus, the workshop was focused on scintillation materials and their applications.

In this workshop, 3 overseas researchers were invited: Dr. M. Zhuravleva (University of Tennessee, United States), Dr. L. Swiderski (National Centre for Nuclear Research, Otwock-Swierk, Poland) and Dr. J. ouzvicka (CRYTUR, Czech).

Dr. M. Zhuravleva studies crystal growth of halide materials [1], and she presented the crystal growth of ternary halide scintillators with high energy resolution.

Dr. L. Swiderski is an expert on the evaluation of the optical and scintillation properties [2], and he showed the evaluation technique how to measure the light yield non-proportionality, energy resolution and scintillation decay time.

Dr. J. Houzvicka is CEO of CRYTUR company which produces single crystals [3]. He talked about the method to prepare 6-inch Y₃Al₅O₁₂ (YAG) crystals, and their application as scintillation materials or lasers.

The participants were 80 persons from 4 countries (Fig. 1) who research in several fields such as material science, radiation physics in academic or industrial fields. During the question time, active discussions were held which significantly contributed to the success of the workshop.



Fig. 1 Photograph of the talk session in the workshop

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Keywords: crystal growth, optical properties

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Activity Report

KINKEN WAKATE



FY 2015 KINKEN WAKATE

No.	Chairperson	Title of Workshop	Place	Date
15Wakate	Prof. Saito	12th Materials Science School for Young Scientists (KINKEN-WAKATE 2015), "Spintronics & Spin Current"	AIMR and Sakunami	2015.9.24-25

Kinken Wakate: "Spintronics & Spin Current"

On September 24-25, Kinken Wakate "Lectures on Spintronics & Spin Current" was held in Sendai as a collaborative activity by ERATO-SQR, Nano Spin Conversion Science, and ICC-IMR. The aim of this program is providing young researchers with cutting-edge reviews of various aspects of spin science and encouraging them to challenge the frontier of this research field.

Spintronics and spin-current are the novel scientific concepts emerging from notable developments of nanotechnology during past two decades. The use of spin and flow of spin are now at the stage of seeking commercial applications and GMR, TMR, and MRAM are spectacular success of such challenges. The aim of this series of lectures is encouraging young researchers to challenge the frontier of spin science and to network with each other for their future collaborations. As a result, about 100 young distinguished researchers and students attended this program and vigorous discussions were exchanged among participants throughout the event. We believe thus established spin science community contributes to the future development of this field of research.

On 24 September Dr. Eiji Saitoh, Director of ERATO-SQR, Tohoku University, delivered an opening remark. His point was that a truly innovative idea came up from people rather than a specific individual and that sharing new concept among researchers like this event would be a timely catalyst for creating innovative ideas.



Fig.1 A scene of opening remark

The lecture started from Dr. Yoshinori Tokura, Riken Center for Emergent Matter Science, titled "Magnetic Skyrmion" covering various research results about Skyrmion physics. Then Dr. Katsuaki Sato, Center of Research & Development Strategy, JST, Dr. Hiromi Yuasa, Graduate School and Faculty of Information Science and Electric Engineering, Kyusyu University, Dr. Jun Hayakawa, Center for Exploratory Research Hitachi, Ltd., Research &Development Group, and Dr. Koki Takanashi, IMR, Tohoku University delivered lectures respectively. The lectures covered many topics from basic to applied research, theoretical to experimental aspect, spintronics to the related fields such as skyrmion.



Fig.2 A scene of lecture

After the lecture, participants moved to Sakunami, western city of Miyagi, to lodge together, and their energetic discussion continued even at dinner time.

Next day (on 25 September), Dr. Eiji Saitoh, and Dr. Shuichi Murakami, Department of Physics, Tokyo Institute of Technology, delivered lectures on spin current and topological phenomena in spintronics. Dr. Naoya Okamoto, Nissan Institute Modern Japanese Studies, University of Oxford talked about his Ph.D. research in physics and carrier and roles of Ph.D. holders in Japan.

Then the closing remark was given by Dr. Shuichi Murakami. He summarized this two-day intensive lectures, and expressed his deep gratitude with all persons involved in this event.

After the event, the participants enjoyed excursions either Nikka whisky factory tour or Tohoku University IMR tour. About 30 people joined this IMR tour with the cooperation of 6 laboratories and Public Relations Office in IMR.

The organizers appreciates kind collaborations of all participants, lecturers and contributors for the success of this lecture.

Keywords: spin current, skyrmion, Spin Hall Effect Eiji Saitoh (AIMR/IMR), Tomohiko Niizeki (AIMR), Yasuyuki Oikawa (AIMR) and Osamu Maegoya (IMR) E-mail: <u>sqr-erato@aimr.tohoku.ac.jp</u> <u>http://www.jst.go.jp/erato/saitoh/index.html</u>

Activity Report

Short-term Visiting Researchers

Application No.		Host	Proposed Research	Title	Affiliation	Term
15SV1	Atsufumi Hirohata	K. Takanashi	Experimental Demonstration of a Persistent Current	Professor	University of York, UK	2015.11.11-17
15SV2	Hendra Hermawan	M. Niinomi	Confronting Biodegradable Metals with the Established Inert Metallic Biomaterials	Assistant Professor	Laval University, Canada	2015.7.19-8.6
15SV3	Jianfeng Zhang	T. Goto	Spark Plasma Sintering of WC- cBN Composites Using SiO ₂ Coated cBN	Professor	Hohai University, China	2015.11.10-18
15SV4	Subhankar Bedanta	K. Takanashi	Magnetization Reversal Processes in Perpendicularly Magnetized FePt Dots and Antidots	Reader in Physics	School of Physical Sciences, National Institute of Science Education and Research (NISER), India	2015.12.7-25
15SV5	Zhenxing Wang	H. Nojiri	High Frequency EPR Study on Magnetic Molecules with Control of Oxidation States	Associate Professor	Wuhan National High Magnetic Field Center	2015.12.14-12.26
15SV6	Yunping Li	A. Chiba	Passivation Mechanism of NiCoCrMo alloy with Cu Addition in HF Acid Solution	Professor	Central South University	2015.12.9-12.19
15SV7	Teimuraz Vekua	H. Nojiri	Magnetic field and Dzyaloshinskii-Mprojy anisotropy effects in frustrated quantum spin chains	Junior Professor	Institute of Theoretical Physics, Leibniz University of Hannover, Germany	2015.2.13-2.27

Short-term Visiting Researchers

Experimental demonstration of a persistent current

A new method to generate a spin-polarised persistent current in a non-magnetic nanoring has been theoretically proposed almost 20 years ago [1]. This method utilises a Berry phase induced in the ring due to a non-uniform magnetic field application onto the system. In this work, we have been developing a nanofabrication process to demonstrate such a persistent current at low temperature.

The quantum phases of charged particles in mesoscopic structures have been investigated intensively. Their interference and oscillatory behaviors were induced by application of an external field [2]. Electrons traveling along semiconductor or normal metal rings threaded by a magnetic flux acquire a quantum dynamical phase that produces interference phenomena such as the Aharonov-Bohm (AB) and Altshuler-Aronov-Spivak (AAS) effects. In addition, when the spin of the electron rotates during its orbital motion along the ring-shaped path, the electron acquires an additional phase element known as the geometrical or Berry phase.

A new nanofabrication method has been developed to produce a quantum device on a MgO(001) substrate consisting of a nonmagnetic nanoring (inner diameter: 200-350 nm) with an FePt nanopillar (diameter: 120-270 nm) inside by a combination of electronbeam lithography and Ar-ion milling. The Cu nanoring is 150 nm wide and 20 nm thick.

As shown in Fig. 1, the center nanopillar is designed to provide a nonuniform magnetic field in the nanoring in its remanent state after perpendicular saturation (device A). Four contacts are fabricated near the nanoring for measurement of the induced current.



Fig. 1 Fabricated quantum device A, consisting of an FePt nanopillars surrounded by a Cu nanoring.

We have also fabricated a new device with 10 nanopillars in line surrounded by a Cu electrode as shown in Fig. 2 (device B). This is similar to the semiconductor device showing a quantum geometrical effect [3] and is anticipated to increase the signal-to-noise ratio for our measurements..



Fig. 2 Fabricated quantum device B, consisting of 10 FePt nanopillars in a line surrounded by a Cu electrode.

We plan to perform the low-temperature measurements at the Toshiba Cambridge Laboratory this summer. An improved device is expected to demonstrate a spin-polarised persistent current, which is absolutely different from the conventional spin-current generation methods. Our devices are also expected to reveal fundamental physics of the spin transport in a geometrically-confined structure.

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Keywords: spin current, magnetoresistance (transport) and nanostructure Atsufumi Hirohata (University of York, United Kingdom) E-mail: atsufumi.hirohata@york.ac.uk http://www-users.york.ac.uk/~ah566/

Spark plasma sintering of WC-cBN composites using SiO_2 coated cBN

Cubic boron nitride is the hardest material only next to diamond and is expected to enhance the hardness and fracture toughness of other cutting materials such as tungsten carbide or alumina. However, the using of Co sintering aid for WC would like to induce the phase transformation of cBN to hBN and lead to a volume expansion resulting in cracking and low hardness of the products. In the present study, SiO₂ nanolayer was coated by a novel rotary CVD method on cBN to depress its phase transformation to hBN. The sinterability and the mechanical properties were also enhanced with SiO₂, indicating that the proposed coating method is promising for developing new cBN-containing cutting tools.

The novel rotary CVD apparatus developed in our group was used [1], with tetraethyl orthosilicate (TEOS) evaporated at 383 K as a precursor, to coat SiO₂ nanolayer on cBN powder (~4 μ m in diameter) at 973 K. Oxygen was also adopted to accelerate the decomposition of TEOS. Fig. 1 shows the typical TEM images of (a, b) cBN and (c, d) SiO₂-coated cBN powders, and SiO₂ nanolayer about 70 nm in thickness was observed to surround cBN uniformly.



Fig. 1 TEM images of (a, b) cBN and (c, d) SiO_2-coated cBN

The as prepared SiO₂-coated cBN was mixed with WC (~60 nm in diameter) by ball milling for 6 h in ethanol using zirconia balls (3 mm in diameter). After drying at 333 K for 24 h, the milled powder was sieved through the 200 mesh, filled into the araphite die of 10 inner diameter, mm in and then consolidated by SPS (SPS-210LX, SPS Syntex Inc.) at 1773 to 2073 K, respectively. The more obvious shrinkage of WC-cBN/SiO₂ composites was found due to the incorporation of SiO₂ nanolayer. And the shrinkage ended after a holding time of about 60s at a sintering temperature of 1873 K, indicating that sintering completed.

Fig. 2 shows the X-ray diffraction patterns

of WC-40vol% cBN/SiO₂ composites sintered at 1773 to 2073 K, respectively, as well as that of the raw powder. The phase transformation of cBN to hBN occurred only at a high sintering temperature of 2073 K, indicating that SiO₂ depressed the phase transformation of cBN effectively. The relative density of WC-cBN composites was increasing increased with also SiO₂ nanolayer content. After sintering at 1873 K, the relative density of WC-cBN was only 82%, but that of WC-cBN/SiO2 was increased apparently up to 96%. Chen et al. coated amorphous SiO₂ layer on SiC whiskers (SiC_w) and Al₂O₃ powder, and found that the amorphous SiO₂ coating improved SiC_w-reinforced densification of Al₂O₃ composites due to the viscous flow of amorphous SiO₂ at a relatively low temperature (\sim 1573 K) [2]. In the present study, the almost full densification of WC-40vol% cBN/SiO₂ may also be attributed to the viscous flow of the amorphous SiO₂ shell coated on cBN core.



Fig. 2 XRD patterns of WC-40vol%cBN/SiO_2 raw powder and composites consolidated at 1773 to 2073 K $\,$

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Keywords: Powder processing; Sintering; Phase transformation Jianfeng Zhang, College of Mechanics and Materials, Hohai University, Xikang Road-1, Nanjing 210098, P.R. China E-mail: jfzhang_sic@163.com

Magnetization reversal processes in FePt antidot arrays

We fabricated FePt antidot lattices with various diameters $d \sim 40$ nm, 100 nm, and 200 nm by electron beam lithography, in which the shapes were designed to be squares, circulars and triangulars. In order to understand the magnetization reversal process in these FePt antidot-arrays, the magneto-optical Kerr effect were measured using the micro-sized laser spot system, and the unique behavior of magnetization reversal was observed.

The L1₀-FePt alloy is one of the most promising materials for future ultrahigh density magnetic storage devices because it possesses a huge uniaxial magnetocrystalline anisotropy (K_u = 7 x 10⁷ erg/cc) which leads to the high thermal stability of magnetization in a nanometer scale. The aim of this international collaboration work is to understand the magnetization reversal processes in thin films, dots and antidots of FePt. In this collaboration, we previously studied the magnetization reversal process in FePt thin films deposited on MgO (110) substrates exhibiting in-plane uniaxial magnetic anisotropy. The thin films were prepared by sputtering in the group of Prof. K. Takanashi, IMR, Tohoku University. It was found that the uniaixal magnetocrystalline anisotropy energy increased with the increase in film thickness and deposition temperature. Domain imaging performed by magneto-optic Kerr microscopy with a longitudinal geometry at NISER, India suggested that the domain structure and magnetization reversal process strongly depended on the film thickness and the deposition temperature. For the films deposited at a certain temperature, there existed a critical thickness where the coercive and saturation fields showed maxima. [1]

Based on the experimental results for the FePt thin films, we investigated the details of magnetization reversal process for nanostructured FePt. Magnetic micro-/nanostructures only are not interesting for fundamental research but they have a high potential for applications. We studied on "negative" magnetic structure that was made using lithography to create a mesh of "holes" in a continuous FePt magnetic thin film. These negative structures are called as "antidots". The array of such antidots is called as "magnetic antidot lattice (MAL)". MALs are receiving intense research interest because of their potential advantages, lack of such as superparamagnetic limit to the bit size (as compared to dot arrays). The domain wall (DW) motion and their dynamics in such MAL system have not been studied so far. The major question is how a magnetic DW will behave in a MAL system where there are periodic defects. Also so far a systematic study on MAL systems for various shape, size and interdot spacing has not been performed. The domain nucleation, domain size and shape will certainly be affected by the shape and size of antidots. In this context, one goal of this collaboration work is to reveal the domain formation and measure the DW velocity as a function of applied magnetic fields with the Kerr microscopy.



Fig. 1: Scanning electron microscopy images of FePt antidot lattices with (a) circular and (a and b), square (c and d), and triangular (e and f) shapes. For each shape we fabricated both 100 and 200 nm size antidots. All images are in same scale and the scale bar is shown in (e).

Keywords: magnetic nanostructures, scanning electron microscopy,

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Short-term Visiting Researchers

It should be noted that magnetization reversal of the perpendicularly magnetized FePt antidots have never been studied. As the first step to reveal the DW dynamics in MALs, we focused on the study of magnetization reversal behavior for L1₀ ordered FePt antidot systems. We fabricated the MALs with various dimensions of the antidots ranging from 200 nm to 40 nm. MAL arrays for various types of lattices such as square and honeycomb were fabricated in order to study the effect of the lattice pattern on the magnetization reversal. Scanning electron microscope (SEM) revealed that the size and shape of the antidot lattices were well controlled. In addition to the perpendicularly magnetized FePt antidots, magnetic antidots of FePt thin films with in-plane anisotropy were prepared.

Fig. 1 shows the SEM images of FePt MALs on MgO (100) substrates with circular, square and triangular shapes.



Fig. 2 Magnetic hysteresis loops were measured by a magneto-optical Kerr effect set-up using the micro-sized laser spot in the longitudinal configuration. Hysteresis loops are shown for (a) the unpatterned film, (b) circular antidots with 100 nm and (c) 200 nm diameter, and (d) triangular antidots with dimension of 100 nm.

Magnetic hysteresis loops were measured using a magneto-optical Kerr effect set-up with the micro-sized laser spot in the longitudinal configuration, which revealed that coercivity in the antidot lattices strongly depended on the size of the antidots (see Fig. 2). In order to understand the domain structure we will perform magnetic force microscope (MFM) under external fields. We are now performing micromagnetic based OOMMF (Object oriented micromagnetic framework) simulations to understand the domain nucleation and domain 2

wall motion in antidote arrays. Kerr microscopy measurements are being investigated on the antidot samples in NISER, India. [2] Also in the framework of this collaboration we have published our work on the interaction induced superferromagnetic domain state in the perpendicularly magnetized FePt dot arrays. [3]

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Solid-to-Solid Progressive Crystal Transformation Involving Ligand Exchange, Solvent Insertion, Air Oxidation, Coordination Re-arrangement and Ferromagnetism to Antiferromagnetism

Introductory part, Abstract: Clear light yellow rhombic crystals of $Fe^{II_4}(mbm)_4Cl_4(MeOH)_4$ (1), (Hmbm = (1-methyl-1H-benzo[d]imidazol-2-yl)methanol) changes their color gradually to opaque black in the atmosphere and converted to $[Fe^{III_4}(mbm)_4(OH)_4Cl_4]\cdot 4H_2O$ (2) through single-crystal-to-single-crystal (SC-SC) transformation. High field electron spin resonance measurements proved that {Fe^{III}_4} cubane of 1 is converted into {Fe^{IIII}_4} cubane of 2 during the SC-SC transformation process.

Solid-to-solid phase transformation, a change of structure, usually occurs as a function of external physical stimuli such as light, temperature, pressure, mechanical force, as well as their synergic effect [1]. In some rare cases, it occurs by chemical reaction without damaging the crystallinity. A survey shows that only 36 examples related to SC-SC transformation start from clusters has been reported. Among these examples. only three examples involving gas-solid redox reaction upon SC-SC transformation were studied

We have synthesized $Fe^{II}_4(mbm)_4CI_4(MeOH)_4$ (1) with the (1-methyl-1H-benzo[*d*]imidazol-2-yl)methanol (H*mbm*) ligand. It is interesting to see observed that the color of the crystals changed through light-yellow, yellow–brown, brown and finally black after exposure in air under ambient condition (Figure 1 top). Crystallography of the black crystal reveals the same {Fe₄O₄} core of a different molecule, [Fe^{III}₄(*mbm*)₄(OH)₄CI₄]·4H₂O (**2**), within a slightly reduced unit cell of the same space-group but with three chemical changes.



Fig. 1 (Top) Optical photograph of fresh Fe₄ after exposure in air for 0, 0.5, 1.5, 24, and 48 h. (Bottom) HF-ESR spectra of 0 h and 48 h samples at various frequencies. Solid lines are the linear fit to each resonance branch.

Structural and magnetization studies indicate there has been oxidation of the Fe(II) to Fe(III). In order to further confirm the charge value of iron ions and study the SC-SC transformation process, high field electron spin resonance (HF-ESR) measurements were carried out on two polycrystalline samples 1 and 2. Fig. 1(bottom) shows the frequency dependence of the HF-ESR spectra at low temperatures. The spectra of the two compounds show very different features: four strong signals were observed for 1, and the linear extrapolations to the resonance fields give three energy gaps of 27, 46, and 190 GHz, implying the existence of large zero-field splitting in 1, consistent with fitting results to $\chi_m T$. Four effective g-values of 1.49, 2.92, 3.61, 5.50 were obtained. The displacements of g-values from 2.00 could be due to the strong spin-orbital coupling within Fe(II), or the occurrence of the level mixing with excited spin states at the high magnetic field (considering the small J_1 and J_2 values) [2]. In contrast, the HF-ESR spectra of 2 contain only two peaks, and the linear extrapolations to the resonance fields give the energy gaps of ~20 GHz with g-values of 2.08 and 2.04. This is consistent with the nature of Fe(III) ions with very small zero-field splittings [2], and is also consistent with the susceptibility analysis, proving that all the iron ions in 2 are Fe(III).

In sum, HF-ESR has proved that $\{Fe^{II}_4\}$ cubane of **1** is converted into $\{Fe^{III}_4\}$ cubane of **2** during the SC-SC transformation process.

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Passivation Mechanism of NiCoCrMo alloy with Cu Addition in HF Acid Solution

A small addition of Cu yielded a tremendous improvement in corrosion resistance of Ni-30Co-16Cr-15Mo-6Fe alloy, even after cold forging. In addition, the passivation of the alloy by a Mo-oxide-dominated passive film was completely changed to passivation by a Cu-dominated one during immersion in hydrofluoric acid solution.

Recent research has indicated that substituting Co for Ni by up to 30 wt.% can greatly increase the strength of the alloy without sacrificing its corrosion resistance to HF solutions [1]. This is made possible by greatly reducing the stacking fault energy (SFE) of the alloy by alternating its plastic deformation mechanism because the cross slip is significantly inhibited in low-SFE materials, leading to higher work hardening of materials and therefore higher hardness or strength. The strength of NiCoCrMo alloy can be further enhanced by cold working, although the corrosion resistance of the deformed NiCoCrMo is greatly reduced in comparison to that of NiCrMo [2]. More recent research indicated that even a small addition of Cu (approximately 2 wt.%) yielded a tremendous improvement in the corrosion resistance of NiCoCrMo, even after severe plastic deformation. However, mechanism the passivation of the Cu-modified alloy has yet been clarified. In present the research, the passivation mechanism of NiCoCrMo alloy modified by 2 wt.% Cu during immersion in HF solution was investigated and discussed in detail.



Fig. 1 SEM images and corresponding EDS elemental mappings in the cross section of the passive film of (a) NiCoCrMo alloy for Ni, Co, Cr, Mo, Fe, O, and C, and (b) NiCoCrMoCu alloy for Ni, Co, Cr, Mo, Fe, Cu, and O after immersion in HF solution (5.2 M) at 100 °C for 100 h.

Fig.1 shows that the passive film of NiCoCrMo alloy is approximately 20 nm in depth and is slightly rich in both Mo and O, and the concentrations of other elements are lower. In NiCoCrMoCu sample, the passive film is rich in Cu, and the O intensity is slightly higher than that of the matrix. It is worth noting that Mo, which is the dominant component in NiCoCrMo alloy, was almost completely replaced by Cu in the film, although its concentration in matrix is low.

From the obtained results, it is evident that the addition of 2 wt.% Cu greatly enhanced the corrosion resistance of NiCoCrMo alloy to HF solution, which is more obvious on the samples subjected to cold forging. Cu demonstrates a positive effect in terms of enhancing the corrosion resistance of the alloy, which is characterized by the extremely low mass loss during immersion testing and a Cu-rich passive film on the sample surface. In addition, such a small addition of Cu completely altered the passivation mechanism of NiCoCrMo alloys passivation from Mo-dominated into Cu-dominated passivation in HF solution.

Although the high resistance of pure Cu and its alloys in HF acid solution has been well known, its tremendous effect even under a minor addition has not been reported extensively. In the presence of Cu, due to the highest standard electrode potentials of Cu (Cu2+/Cu, 0.342 V) Cu does not react with HF acid solution, and with the progress of selective leaching of other elements from the alloy in HF solution into stable ions, Cu segregated as a compact film on the out most surface of sample. This would be the predominant reason for the inhibiting effect of Mo fluorides by Cu.

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Activity Report

Young Researcher Fellowships



No.	Name	Host	Proposed Research	Title	Affiliation	Term
15FS1	Benedikt Johannes Hartmann	T. Sasaki	Investigation of Low-Frequency Charge and Spin Dynamics in Correlated p-Electron Systems with Multi-Degrees of Freedom	Research Assistant & PhD Student	Institute of Physics, Goethe- University Frankfurt, Germany	2015.5.14-7.18
15FS2	Yi Liu	M. Niinomi	Absorption Behaviors of Serum Proteins on the Surfaces of Biomedical Titanium Alloys	Assistant Professor	Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China	2016.1.6-3.6

Investigation of Low-Frequency Charge and Spin Dynamics in Correlated π -Electron Systems with Multi-Degrees of Freedom

Recently, in the family of molecular conductors it has been shown that electronic states can be reversible set by utilizing the inherent glassy character of the materials. In θ -(BEDT-TTF)₂RbZn(SCN)₄ crystallization can be kinetically avoided when quenching the system after applying a heat pulse, thus a charge glass can be realized. The origin of the charge glass-crystal transition still demands a detailed transport investigation.

We have demonstrated that the partially deuterated molecular conductor к-(d_{0.8}/h_{0.2}-BEDT-TTF)₂Cu[N(CN)₂]Br (к-Br) can be tuned across a Mott transition by utilizing its inherent glass-like properties [1]. While coupled to a low temperature heat bath a heat pulse is applied and after switching it off the local temperature rapidly relaxes and introduces a Mott insulating state [2]. By partially relaxing the material at the glass-like temperature $T_g=75$ K it is possible to realize any state between the Mott insulator and the complete relaxed metallic/superconducting state [1]. Applying a heat pulse quench to a similar material θ-(BEDT-TTF)₂RbZn(SCN)₄ (θ-RbZn) it enters a charge glass state, which can analogues to $\kappa\text{-}Br$ reversibly relaxed into a charge crystal. The charge glass state has been investigated by optical conductivity

measurements on a compound in the same

family θ-(BEDT-TTF)₂CsZn(SCN)₄ [4]. In order to study the charge glass state and its transition to the charge crystal state by optical conductivity, there are certain experimental requirements to fulfill. The cryogen free optical cryostat in use for the optical conductivity measurement is not capable of realizing rapid cooling rates. Therefor the heat pulse method has been considered to realize the desired ground states in θ -RbZn. This demands some modifications compared to usual measurements: the sample holder has to be insulating to avoid shortcutting the conductivity measurements, but still has to thermally couple the sample to the cryostat. Therefore a sapphire plate has been chosen, which has further been equipped with a small resistor. It can be used to locally implant a heat pulse alternatively to the sample itself, which is more difficult to control, because of its large dR/dT. The proof of principle has been demonstrated and is shown in figure 1. After a heat pulse the red curve (charge glass state) has been measured. Waiting certain times in the temperature range 150-220 K relaxes θ-RbZn away from the charge glass towards the charge

crystal state (green and yellow curve). In addition the first order character of the transition to the charge crystal state is visible by



Fig. 1 Resistance of θ -RbZn for a temperature protocol.

the large and abrupt resistance jump and a wide hysteresis. The charge crystal (or charge ordered) state is difficult to avoid for the first cooldown of the system because no pulse method is applicable. Therefore usually the sample undergoes the first order transition. This often leads to sample breaking or at least misalignment due to tension coming from electrical wires. Nevertheless first reflectivity data has been collected and a guideline for an optimized procedure has been established.

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