



**International  
Collaboration  
Center**

Institute for Materials Research  
Tohoku University

# ICC-IMR FY2011 Activity Report

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ICC-IMR FY2011

# Activity Report

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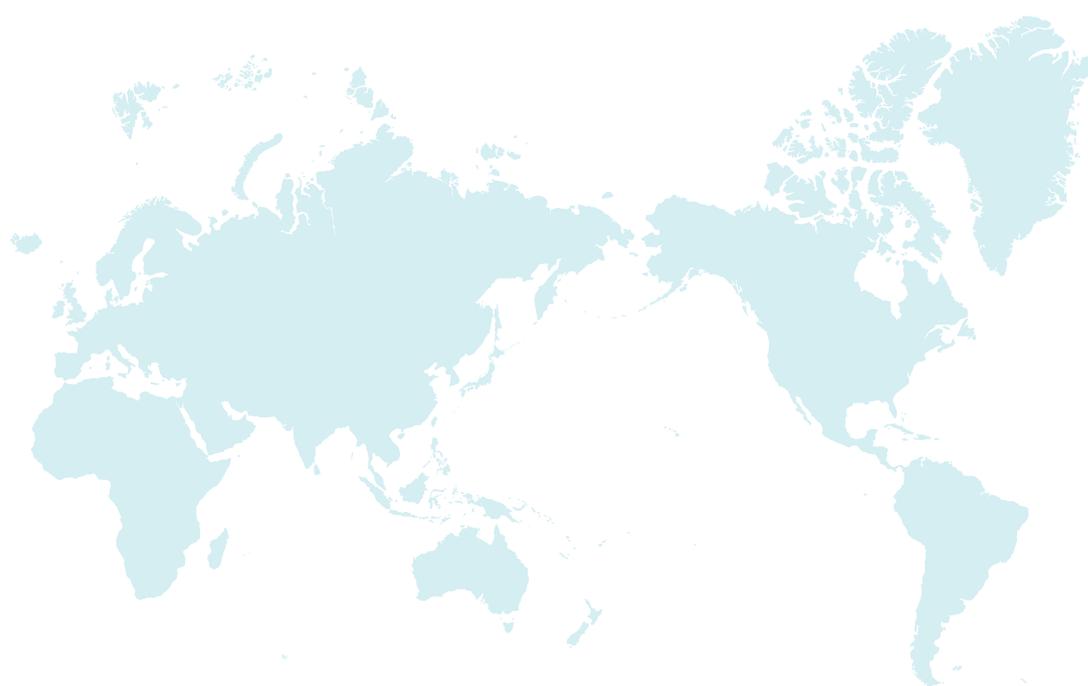
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## Mission

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 25 visiting professors and conducted 11 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!

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Activity Report

# Visiting Scholars



## FY 2011 Visiting Scholars

No.	Candidate	Host	Proposed Research	Title	Affiliation	Term
11G1	Chuang Dong	A. Chiba	Cluster-Plus-Glue-Atom Model for Low-E $\beta$ -Ti bio-Alloys	Professor	Dalian University of Technology, China	2011.10.31-11.30
11G2	Czesław Z. Rudowicz	H. Nojiri	Study of the Role of the Higher-Order Field-Dependent (HOFD) Terms in Characterization of Magnetic, Optoelectronic, and Laser Materials	Professor	West Pomeranian University of Technology, Pola	2011.10.1-11.30
11G3	Claude Berthier	H. Nojiri	High Field NMR on Quantum Phase Transition	Director of Research Emeritus	CNRS, France	2011.10.1-10.31
11G4	Krishnan Baskar	T. Matsuoka	Growth and Characterization of Alloys of GaN, InN and AlN for Optoelectronics	Professor	Anna University, India	2011.9.21-10.20
11G5	Jian-Tao Wang	Y. Kawazoe	Large-Scale Simulation on Novel Nanoscale Materials	Professor	Institute of Physics, Chinese Academy of Sciences, China	2011.7.22-10.19
11G6	Lei Wang	M. Niinomi	Improvement of Mechanical Properties of TNTZ in Simulated Body Fluid by Controlling of Grain Boundary	Professor	Northeastern University, China	2011.7.1-8.29
11G7	Marcel H.F. Sluiter	Y. Kawazoe	Large-Scale Simulation on Novel Nanoscale Materials	Professor	Delft University of Technology, The Netherlands	2011.6.15-8.5
11G8	Scott P. Beckman	Y. Kawazoe	Exploration of Lead-Free Ferroelectric/Piezoelectric Ceramics from First-Principles	Assistant Professor	Iowa State University, USA	2011.6.1-8.31

## $\beta$ -Ti bio-alloys with low Young's moduli interpreted by cluster-plus-glue-atom model

*$\beta$ -Ti biomedical alloys with low Young's moduli require multiple alloying using both BCC stabilizers and low- $E$  elements. I attempted to introduce the cluster-plus-glue-atom model in the composition interpretation of Ti-Zr-Mo-Nb-Sn alloys. I found out quite interesting composition rules in terms of valence electron concentration and atomic size.*

Ti-based alloys are useful biomaterials for their low Young's modulus (low- $E$ ), high strength, excellent biocompatibility and corrosion resistance [1]. They usually have BCC  $\beta$ -Ti structure containing multiple non-toxic elements such as Mo, Nb, Ta, Zr, etc. The alloying elements play two major roles apart from being non-toxic: stabilizing the BCC structure and decreasing the Young's modulus of  $\beta$ -Ti alloys.

In light of our cluster-plus-glue-atom model [2,3], we here attempt to obtain the composition formula of the low- $E$   $\beta$ -Ti solid solution alloys with high structural stabilities.

According to enthalpies of mixing  $\Delta H$ 's, the cluster-plus-glue-atom model specific to Ti-Zr-Mo-Nb-Ta-Sn BCC  $\beta$ -Ti alloys is proposed as  $[(\text{Mo},\text{Sn})_1(\text{Ti},\text{Zr})_{14}]\text{Nb}_x$ . Alloys conforming to composition formula were prepared at Dalian and the data on BCC stability and mechanical properties were collected there.

The correlations between the  $E$  value and elemental properties such as valence electron concentration and average atomic size were analyzed and summarized in Fig. 1.

Two conclusions can be drawn from this figure. First, all the low- $E$  alloys, both ours and from the literature, are located in the same narrow region, with valence electron concentration per atom being 4.1~4.3 and average atomic size being 0.145~0.148 nm. Second, the alloys showing the lowest  $E$  values are further grouped towards the lower edges of the composition region. It is interesting to note that the latter zone is quite close to that of pure Ti, with valence of 4 and atomic radius of 0.146nm. This figure then points out a practical way to design Ti-based biomaterials with low Young's moduli, by controlling the overall valency of the alloy to about 4.1 and the average atomic radius to about 0.146-0.147nm.

Besides the research, I have visited a few professors, including Dr. W Zhang, Dr. YM Wang, Dr. Nojiri, and Dr. Nakai.. In particular, the discussion with Dr. Nakai was quite useful to guide our future alloy design work. I also gave an open seminar (Fig. 2), entitled "Composition formulas of multi-component complex alloys issued from the cluster-plus-glue-atom model", which was attended by an audience of about forty.

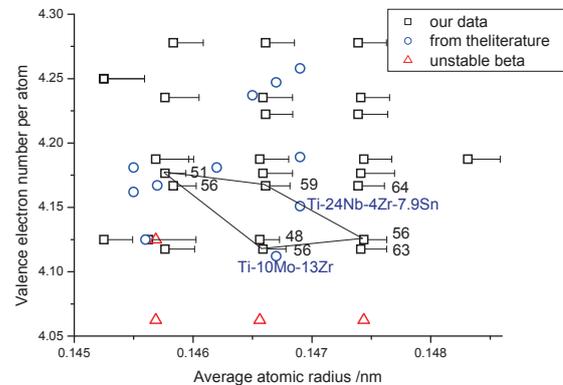


Fig. 1 Compositions of low- $E$  alloys in a 2D map coordinated by valence electron concentration and atomic size. The data are both from our experiment ( $\square$ ) and from the literature ( $\circ$ ). The non-BCC alloys are marked with  $\triangle$ . The Young's moduli  $E$  below 65GPa are shown near the alloy compositions.



Fig. 2 NEDO Lab. Special Lecture on Nov. 29, organized by Dr. Yamaura and Dr. Zhang,

### References

- [1] M. Niinomi, Mater. Sci. & Eng. A 243, 231 (1998).
- [2] C. Dong, Q. Wang, J.B. Qiang, Y.M. Wang, N. Jiang, G. Han, Y.H. Li, J. Wu and J.H. Xia, J. Phys. D Appl. Phys., 40, 273 (2007).
- [3] J. Zhang, Q. Wang, Y.M. Wang, C.Y. Li, L.S. Wen and C. Dong, J. Mater. Res. 25, 328 (2010).

### Key Words

Ti alloys, solid solution model, Young modulus

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## Study of Higher-order Terms in Spin Hamiltonian

We have examined theoretically the role of the higher-order terms in spin Hamiltonians for transition ions (e.g. Cr, Ni, Fe) in various magnetic systems and overviewed experimental studies. The high magnetic fields (**B**) up to 100 T make the non-linear field-dependent terms:  $B^2S^2$ ,  $B^3S$ ,  $B^5S$  &  $B^2I^2$ ,  $B^3I$ ,  $B^5I$ , important.

This study aims at providing theoretical and computational support for researchers working in the area of magnetic, optoelectronic, and laser materials. Two novel methods of characterization of such materials are the high-magnetic field (**B**) measurements (HMM) of magnetic properties as well as the high-magnetic field & high-frequency EMR (HMF-EMR) measurements of spectroscopic properties [1]. The HMF-EMR techniques offer several advantages over the conventional methods, e.g. unprecedented spectral resolution and detection of new phenomena and spectral features, not detectable in X- or Q-band EMR [1-5]. By the higher-order field-dependent (HOFD) terms in the generalized spin Hamiltonians (GSHs) for transition ions we mean the higher-rank terms in the electronic (**S**) and nuclear spin (**I**), i.e. the terms non-linear in **B** of the type:  $B^2S^2$  [5],  $B^3S$  [4] (see, Fig. 1),  $B^5S$  or  $B^2I^2$ ,  $B^3I$ ,  $B^5I$ . The high pulsed fields, up to 100 T achievable at present [2], make these terms significant in comparison with the linear Zeeman electronic (Ze) term **B.g.S**, even if the associated parameters are small. Till recently these terms were mostly omitted from experimental considerations. We have carried out feasibility study on the role of the HOFD terms in HMM and HMF-EMR experiments [6].

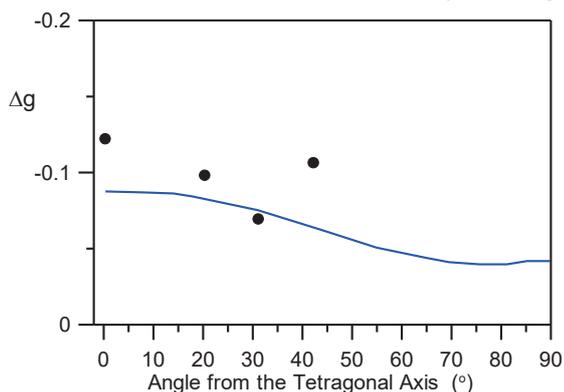


Fig. 1. First experimental evidence of the  $B^3S$  term in GSH observed in the g shift measured at 119  $\mu\text{m}$  – adapted from [4].

The key issues involved in the SH approaches (see, Fig. 2) are: analysis of the mechanisms contributing to the HOFD parameters using microscopic SH (MSH); theoretical prediction of forms of various HOFD terms in GSH using the constructional SH approach; the role of the HOFD terms in the low- and high-field EMR; development of the computer simulation and fitting programs incorporating the HOFD terms; interpretation of the HMF-EMR spectra for the transition ions including HOFD

parameters. Potential applications concern, e.g.,  $\text{Fe}^{2+}:\text{CdPS}_3$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+}:\text{LiNbO}_3$ ,  $\text{GaAs}:\text{In}:\text{Cr}$ ,  $\text{Mn}_{12}$ -acetate, and  $\text{Cr}^{2+}/\text{Cr}^{3+}:\text{forsterite}$ . The preliminary research at IMR has provided a blueprint for future theoretical and experimental studies of the HOFD terms aimed at solving the pertinent theoretical and computational problems. The large scale project would have (i) direct applications for improving spectroscopic characterization of technologically important materials, and (ii) prime scientific importance for advancement of our knowledge. Collaboration of researchers from Japan and Poland is envisaged.

### Constructional SH approach

Point symmetry group  $\Rightarrow$  Group Theory  $\Rightarrow$  Invariant combinations of the spin (**S**) & other operators (**B**, **I**):

$\Rightarrow$  Generalized SH (GSH)  $\propto$  (ZFS, Ze, HOFD terms)

◆ Forms of SH predicted, including zero-field splitting (ZFS), Zeeman electronic (Ze), higher-order field-dependent (HOFD) terms, but no information on the parameter values

### Derivational SH approach

$H_{\text{physical}}(\text{FI}+\text{CF}) \Rightarrow$  Perturbation Theory (PT)  $\Rightarrow$  effective SH:

$\Rightarrow$  Microscopic SH (MSH):  $\propto$  (physical parameters)

◆ Forms of SH and values of ZFS & Ze parameters predicted

Fig. 2. Conceptual framework underlying the two SH approaches (for detailed explanations and references, see [6]).

### References

- [1] M. Motokawa, Rep. Prog. Phys. 67, 1995 (2004).
- [2] Y. Imanaka, N. Miura, H. Nojiri, et al. Physica B246-247, 561 (1998).
- [3] M. Hagiwara, T. Kashiwagi, S. Kiura, et al. J. Mag. Magn. Materials 310, 1272 (2007).
- [4] S. Kuroda, M. Motokawa, M. Date, J. Phys. Soc. Japan 44, 1797 (1978).
- [5] Aripin, S. Mitsudo, T. Shirai, et al., I. J. Infrared & Millimeter Waves 20, 1875 (1999).
- [6] C. Rudowicz, plenary presentation, II Forum EMR-PL, Hucisko, 16-18 May 2012; review, *submitted*, Nukleonika, 2012.

### Key Words

Higher-Order Field-dependent Terms, Generalized Spin Hamiltonians, Electron Magnetic Resonance

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## NMR in Condensed Matter Physics in High Magnetic Field

We have examined the temperature dependence of the relaxation rate in the mix-valence Re-Complex and found a characteristic temperature dependence of  $T_1$  around the expected charge order temperature. We also have discussed a strategy to investigate the high field phases in several strongly correlated systems by the complementary use of NMR and neutron.

NMR is one of the useful methods to examine dynamical and static correlations in strongly correlated electron systems. It is unique in the capability of experiments in very high magnetic fields above 30 T. In fact, it has been used in the studies of interesting high magnetic field phases in quantum magnets, heavy fermion systems and unconventional superconductors.

During the stay in Sendai, I have conducted following three tasks, (1) consulting of NMR activity in the high magnetic field center of IMR, (2) study of mix-valence Re-Complex and (3) discussion of a strategy to examine the high magnetic field phases by neutron diffraction. These tasks have been completed successfully due to my experience as the head of NMR group of the Grenoble High Magnetic Field Laboratory (now called LNCMI) and deputy director of this laboratory. My research activity in the last ten years has been mainly bearing upon condensed matter systems in which the magnetic field plays the role of thermodynamic variable able to induce phase transitions. I paid particular attention to the case of quantum phase transitions, which occurs at  $T = 0$ . These experiences have contributed much to improve the activities of researches in high magnetic field at IMR.

### (1) Dynamics of mix-valence Re-Complex

A complex  $\text{Re}_2\text{Cl}_4(\text{P}_n\text{Pr}_3)_4(\text{Hbim})$  (bim) has a linear structure of Re-H-Re and the two Re ions are in the mixed valence state at room temperature. By lowering temperature, a charge order of Re ions associated with the shift of the hydrogen : H has been conjectured. The shift of the H atom and the change of charge distribution were found by X-ray diffraction experiments, which suggest the charge ordering. However, the X-ray result can be possibly understood by the superposition of the two dynamically charge imbalance. This realizes if the charge fluctuation frequency is much slower than the time window of X-ray. As such, a supplemental information has been required to prove the charge ordering.

Figure 1 shows the tentative analysis of  $\text{P}^{31}$  NMR. Phosphorus ions are located at the apical positions around Re ions. The enhancement of inverse  $T_1$  is found in the temperature range between 100-10 K. Such enhancement is possibly caused by the slowing down of the Re spin fluctuation by the charge

ordering process. The appearance of dynamical anomalies support the charge ordering found by X-ray diffraction. A more detailed analysis and the complementary experiments are in progress.

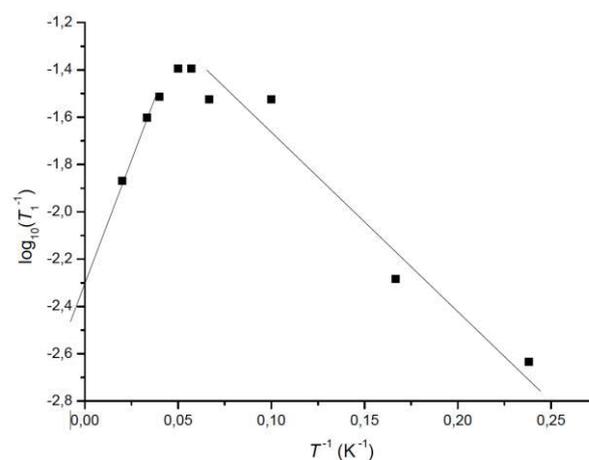


Fig. 1 Temperature dependence of  $1/T_1$  of  $\text{P}^{31}$  nuclear spin. The enhancement is found in the intermediate temperature.

### (2) Strategy for the high magnetic field neutron diffraction

We have examined the magnetic field induced ordering : Bose-Einstein condensation of triplons in the so-called Han Purple compound ( $\text{BaCuSi}_2\text{O}_6$ ) [1]. The quantized plateau state in two-dimensional frustrated antiferromagnet  $\text{SrCu}_2(\text{BO}_3)_2$  was also examined[2]. These two systems require experiments in resistive magnets and very low temperature. We have discussed in details about the possible magnetic structures appearing in these compounds and possibility of neutron diffraction to detect those structures. The strategy would help much for the future neutron diffraction experiments on these compounds by using IMR portable high magnetic field system.

We have also discussed about the upgrade of NMR system. In particular, the automation of scanning is crucial for the effectiveness of the user experiments. The consulting will continue to help the improvement of the IMR facility.

### References

- [1] S. Krämer *et al.*, Phys. Rev. B **76**, 100406(R) (2007).
- [2] M. Takigawa *et al.*, J. Phys. Soc. Japan **79**, 011005 (2010) and references therein.

### Key Words

Higher Magnetic Field, NMR, Proton Dynamics

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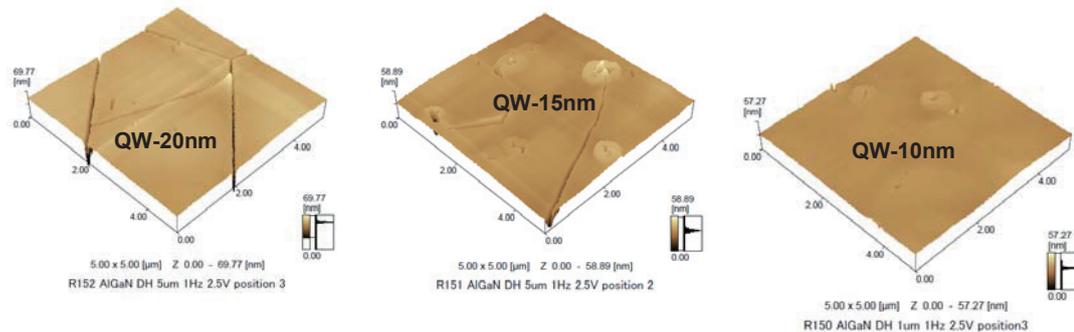
**Report of the work done by Prof.K.Baskar for the period  
20 september 2011 – 21<sup>st</sup> October 2011 at Institute for Materials Research (IMR),  
Tohoku University, Sendai, Japan**

Laboratory tour at Prof.Matsuoka laboratory has been arranged and had detailed discussions about the facilities available for the growth of InGaN materials on sapphire substrates. Two MOVPE systems are being used to grow InN and InGaN materials. The epitaxial layers are analysed by High resolution X-ray diffraction (HXRD), Photoluminescence (PL), Infrared reflectance spectroscopy, Scanning Electron Microscopy (SEM), Atomic force microscopy (AFM), and Hall measurement system. The special growth conditions, such as temperature, high V/III ratio and high reactor pressure required for the growth of good quality indium based nitrides have been discussed. The in-situ monitoring system, such as Laytech tool, required for the understanding of growth mechanism of indium nitride in MOVPE particularly the shape of the initial stage nucleation and their coalescence at higher temperature to obtain two dimensional growth have been discussed. The possible solar cell structure of InGaN for high efficiency solar cells, particularly the issues related to p-type doping and advantage to have concentrated solar cell applications due to strong bond strength between nitrogen and indium and small changes in the bandgap with temperature have been discussed.

AlGaN samples with aluminium content from twenty to seventy percent prepared by MOVPE on a two inch sapphire substrate have been cut into one square centimetre and one by two centimetre square size samples using a diamond scribe.

The samples were cleaned in acetone and isopropyl alcohol. Indium contacts were used to measure the carrier concentration and mobility using four probe method. Though the samples are undoped they exhibited n-type conduction with a carrier concentration of the order of  $10^{17} \text{ cm}^{-3}$  up to the aluminium content of thirty five percent. The higher aluminium content samples above forty percent have shown highly resistive and also difficult to measure the conduction type. The AlGaN/GaN samples with aluminium content of twenty two percent and thickness of around 80 nm have shown two dimensional electron gas (2-DEG) with a mobility of  $980 \text{ cm}^2 \text{ V/sec}$ . The growth of high aluminium content samples on GaN surface is a challenge to grow without cracks and good crystalline quality due to three percent lattice mismatch between AlN and GaN. The

samples have been analysed by scanning probe microscopy. The smooth atomic surface steps, pinholes and micro-cracks have been observed depending on the aluminium content. A typical microstructure of a  $\text{Al}_y\text{Ga}_{1-y}\text{N}/\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{Al}_y\text{Ga}_{1-y}\text{N}$  double heterostructures (DH) on  $\text{GaN}/\text{Al}_2\text{O}_3$  observed in AFM is shown in figure.



**Figure..The surface morphology of AlGaN-DH with various thickness of active layer**

Though the thickness of GaN buffer layer and  $\text{Al}_y\text{Ga}_{1-y}\text{N}$  barrier is the same, a small variation of 5 nm thickness resulted in micro-cracks and the cracks terminate at the pinholes. The micro-cracks are formed due to relaxation of strain once the critical thickness of active layer of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  exceeds the limit. Attempts have to be made to grow high aluminium content ( $\text{Al} > 40$  percent) contained AlGaN with crystalline quality and smooth morphology using AlN buffer with a better lattice match. Once the conditions are optimized for the AlGaN layers, the doping issues particularly p-type doping will be undertaken for the development of high efficiency ultraviolet light emitting diodes.

To promote academic exchange and cooperative research, visits were made to the following universities in Japan, Nagoya Institute of Technology, Hiroshima University, Kyushu University and Hokkaido University during 14-20 October 2011. In general all universities are eager to establish and strengthen the bilateral academic and research cooperation with Anna University, Chennai, India. As there are large number of Japanese companies in Chennai and also discussions are going on between government of Japan and Government of Tamilnadu in Chennai, India, to establish a Japanese industrial park in Chennai many institutions are looking for a trilateral cooperation between industry in Japan or India and academia of Japan and Anna University. In this connection the future

visits are expected from Hiroshima University and Kyushu University through the MEXT programme of Japanese government. Extensive discussions were made to strengthen the semiconductor research at Crystal Growth Centre of Anna University. In this connection it is proposed to have a Indo-Japan joint workshop on nitride semiconductors for electronics, photonics and photovoltaic applications in the year 2012 so that the researchers in Japan and India can join the workshop in Anna University to bring out joint deliberations on future strategy to establish strong collaborations between Indian universities/institutions and Japanese universities. The deliberations will also be useful to strengthen the research on nitride semiconductors for the development of novel devices.

The organisers of the Ceremony of the declaration of international material science week 2011 on 11<sup>th</sup> October 2011 at IMR, Sendai, have invited me to participate and give a brief talk. The director of IMR, professors and researchers from IMR and abroad have participated in the programme.

It was a wonderful opportunity to share some of my thoughts about the recent disaster in Fukushima, the collaborative research between IMR and Anna University, the new initiatives in the development of materials at Anna University and other things for a better future and sustained mankind.

I am thankful to IMR particularly Prof. T. Matsuoka and Anna University, India, for their support to establish active collaboration, characterisation of AlGa<sub>0.5</sub>N and also to develop InGa<sub>0.5</sub>N for solar cell applications.

## Orthorhombic Carbon Allotrope of Compressed Graphite

We identify by *ab initio* calculations an orthorhombic carbon (O-carbon) in *Pbam* symmetry for compressed graphite in AA stacking, which is formed via a distinct one-layer by one-layer slip and buckling mechanism along the [210] direction. The O-carbon is comparable to diamond in ultralow compressibility, has a band gap wider than that of diamond, and is compatible with experimental x-ray diffraction data.

Experimentally, an unquenchable transparent and hard phase has long been observed during the cold-compression (at room temperature) stage of the synthesis. Recent studies have identified several structural forms for cold-compressed graphite, including a monoclinic M-carbon and an orthorhombic W-carbon, which provide a critical link for the graphite-to-diamond transformation [1]. In this Report, we identify by *ab initio* calculations an O-carbon allotrope in *Pbam* symmetry, which is formed via a one-layer by one-layer slip and buckling along the [210] direction [2]. This transformation mechanism is distinct from mechanisms previously proposed for M- and W-carbon that occur along the [100] direction [3]. Its simulated x-ray diffraction pattern matches well the experimental data on compressed graphite. The O-carbon has a band gap wider than that of diamond and a bulk modulus comparable to that of diamond. It is more stable than W- and M-carbon energetically. These results broaden our understanding of the complex structural landscape of compressed graphite and provide insights into the relations among the rich variety of carbon allotropes.

The crystal structure of O-carbon with the space group *Pbam* is shown in Fig. 1(a). It can be considered as distorted graphite in an AA stacking. At zero pressure, the equilibrium lattice parameters are  $a = 4.755 \text{ \AA}$ ,  $b = 7.786 \text{ \AA}$ , and  $c = 2.494 \text{ \AA}$  with four inequivalent crystallographic sites, occupying the 4h (0.1072, 0.0706, 0.5), 4h (0.3614, 0.9546, 0.5), 4g (0.9632, 0.8267, 0.0), and 4g (0.3090, 0.8436, 0.0) positions, respectively. At high pressures, O-carbon becomes stable relative to graphite above 11.15 GPa [Fig. 1(b)], and it is more stable (i.e., lower in enthalpy) than both M-carbon and W-carbon.

Figure 1(c) shows the calculated band structure of O-carbon at 15 GPa using the hybrid functional (LDA-HSE06) that produce the band gap in good agreement with experimental data for diamond. The valence band top and the conduction band bottom of O-carbon are both at the point; the calculated band gap is 5.87-6.04 eV over a wide pressure range of 0-25 GPa, which is close to 5.69 eV for W-carbon, but markedly larger than 4.78 eV for M-carbon; it is even appreciably larger than the gap (5.43 eV) for diamond [2]. Therefore, O-carbon is

expected to be optically transparent like M-carbon and W-carbon. We have also calculated its phonon dispersion curves over a wide pressure range up to 60 GPa. No imaginary frequencies were observed throughout the entire Brillouin zone [see Fig. 1(d)], confirming the dynamical stability of the O-carbon phase.

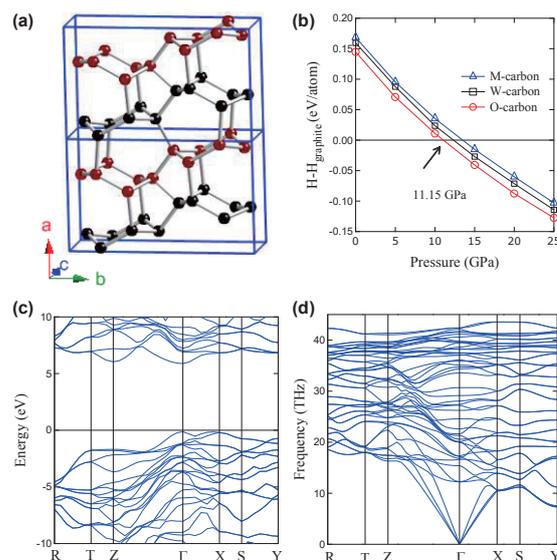


Fig. 1 The orthorhombic O-carbon in *Pbam* symmetry. (a) A polyhedral view of the crystal structure. (b) The enthalpy per atom (relative to that of graphite) for M-carbon, W-carbon, and O-carbon versus pressure. (c) Calculated electronic band structure of O-carbon at 15 GPa; (d) Calculated phonon dispersion curves of O-carbon at 15 GPa.

### References

- [1] J. T. Wang, C. F. Chen, and Y. Kawazoe, *Phys. Rev. B* 84, 012102 (2011).
- [2] J. T. Wang, C. F. Chen, and Y. Kawazoe, *Phys. Rev. B* 85, 033410 (2012).
- [3] J. T. Wang, C. F. Chen, and Y. Kawazoe, *Phys. Rev. Lett.* 106, 075501 (2011).

### Key Words

Carbon, Graphite, Diamond, Phase transformation.

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## Development of novel titanium alloys with changeable Young's modulus for spinal fixation rods applications

**[Introduction]** Implanting metallic rods plays an important role in the treatment of scoliosis et al. [1]. However, the demands of surgeons and patients in terms of Young's modulus are opposite. In this study, deformation-induced phase transformation was taken advantage of to meet the demands of both surgeons and patients.

**[Alloy design]** The novel alloys in this study were designed by Mo equivalents ( $M_{o_{eq}}$ ) [2], as shown in eq. (1), in the metastable range,  $5 \leq M_{o_{eq}} \leq 7$  (mass%) because the deformation-induced phase transformation will occur in the range of  $M_{o_{eq}}$  in the previous report [3].

$$M_{o_{eq}} = [Mo] + [Ta]/5 + [Nb]/3.5 + [W]/2.5 + [V]/1.5 + 1.25[Cr] + \dots \text{ (mass\%)} \quad (1)$$

Based on above concept, Ti-30Zr-4Cr, Ti-30Zr-5Cr, Ti-30Zr-1Cr-5Mo, Ti-30Zr-2Cr-4Mo, and Ti-30Zr-3Cr-3Mo alloys, which  $M_{o_{eq}}$  are 5.00, 6.25, 6.25, 6.50, and 6.75, respectively, (hereafter, these alloys are denoted by 4Cr, 5Cr, 1Cr5Mo, 2Cr4Mo, and 3Cr3Mo, respectively) were designed.

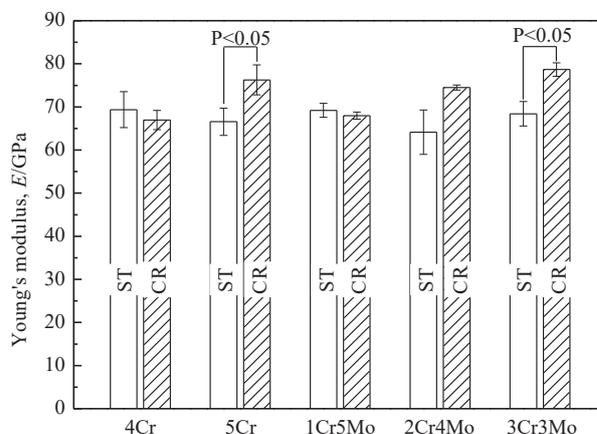
**[Materials and methods]** The designed alloys (Ti-30Zr-(Cr, Mo)) were prepared by arc melting with a non-consumable tungsten electrode under a high purity argon atmosphere. The ingots obtained were homogenized at 1373 K for 21.6 ks and then hot rolled into plates with a reduction ratio of around 70% at 1273 K (both processes were heated in an argon atmosphere), after which ice-water quenching and air cooling were carried out. Then the hot rolled plates were solution treated in vacuum at 1123 K for 3.6 ks and quenched in ice-water. Some of the solutionized plates were cold rolled with a reduction ratio of around 10% at room temperature. As the final treatment, the solution treatment and cold rolling were labeled as ST and CR, respectively. The phase constitution was identified by X-ray diffraction (XRD) analysis. The microstructures were observed by optical microscopy (OM) using a differential interference contrast microscope, electron backscattered diffraction (EBSD) analysis and transmission electron microscopy (TEM). The mechanical properties were evaluated by Young's modulus measurements, tensile tests, and tensile loading-unloading tests.

**[Results and discussion]** After solution treatment, each of the Ti-30Zr-(Cr, Mo) alloys consists of equiaxed  $\beta$  phase and tiny dispersive  $\omega$  phase, which were observed by TEM. The intensity of the athermal  $\omega$  phase decreases with increase in the Mo equivalence.

After cold rolling with reduction ratio of 10%, deformation-induced phase transformations occurs in all the alloys; the deformation-induced products in Ti-30Zr-4Cr, Ti-30Zr-1Cr-5Mo, Ti-30Zr-2Cr-4Mo, Ti-30Zr-3Cr-3Mo are deformation-induced  $\alpha'$  phase and deformation-induced  $\{332\}\langle 113 \rangle$  mechanical twin. The ratio of amount of deformation-induced  $\alpha'$  phase to deformation-induced  $\{332\}$

$\langle 113 \rangle$  mechanical twin decreases with increase in the Mo equivalence. On the other hand, in Ti-30Zr-5Cr, only the deformation-induced  $\{332\}\langle 113 \rangle$  mechanical twin and planar slip can be observed. The results of TEM observation indicates that deformation-induced  $\omega$  phase transformation mainly occurs accompanying with the deformation-induced  $\{332\}\langle 113 \rangle$  mechanical twinning.

Figure 1 shows the Young's moduli variation of each alloys subjected to solution treatment and cold rolling. All the novel designed alloys exhibits low Young's moduli of  $<70$  GPa; this value is much lower than those of SUS 316L stainless steel (SUS 316L), commercially pure titanium (CP Ti), and Ti-6Al-4V ELI alloy (Ti64 ELI) [3], which are currently widely used for spinal fixation applications. After cold rolling, the Young's moduli of 4Cr and 1Cr5Mo decreased slightly compared with those under ST conditions. However, the Young's moduli of 5Cr, 2Cr4Mo, and 3Cr3Mo increased by cold rolling, with those of 5Cr and 3Cr3Mo increasing in the range of  $P < 0.05$ . The Young's modulus of 3Cr3Mo after cold rolling increases to around 80 GPa with an increase ratio of 15%. In Ti-30Zr-Cr-Mo alloys, the difference between the Young's moduli under ST and CR conditions varies with the phase constitution. As mentioned above, under CR conditions, the amount of deformation-induced  $\alpha'$  phase decreases with an increasing in the Mo equivalent; the deformation-induced  $\alpha'$  phase disappears in 5Cr. It is reported that the  $\alpha'$  phase exhibited a lower Young's modulus than that of  $\beta$  phase [4, 5]. Therefore, the decreasing of the Young's moduli of 4Cr and 1Cr5Mo after cold rolling could be attributed to the deformation-induced  $\alpha'$  phase. In the cold rolled 5Cr, 2Cr4Mo, and 3Cr3Mo alloys, since the  $\{332\}\langle 113 \rangle$  mechanical twin can be found, the increasing of the Young's moduli are considered to be related to the  $\{332\}\langle 113 \rangle$  mechanical twin. It is clear that the deformation-induced  $\omega$  phase transformation frequently occurs accompanying with the deformation-induced  $\{332\}\langle 113 \rangle$  mechanical twinning. It is known that the Young's modulus of  $\omega$  phase is higher than that of other phases in



titanium alloys. Therefore, the increasing of Young's moduli in 5Cr, 2Cr4Mo, and 3Cr3Mo after cold rolling are attributed to the deformation-induced  $\omega$  phase.

Fig. 1 Young's moduli of Ti-30Zr-(Cr, Mo) alloys subjected to solution treatment (ST) and cold rolling (CR).

**[Summary]** In summary, after solution treatment, Young's moduli of the alloys are lower than those of the conventional alloys such as SUS 316L, CP Ti, and Ti64 ELI, which offers the possibility to prevent the stress-shielding effect after surgery. After deformation, Young's moduli increases with deformation-induced  $\omega$  phase, which provides the possibility to suppress the springback. Fig. 2 shows the springback of 3Cr3Mo with deformation-induced  $\omega$  phase and TNTZ, without any deformation-induced  $\omega$  phase transformation. The loading-unloading tests indicate that the springback of Ti-30Zr-3Cr-3Mo with deformation-induced  $\omega$  phase transformation is smaller than that of TNTZ without deformation-induced phase transformation. In addition, the tensile properties of Ti-30Zr-3Cr-3Mo show a good balance, providing potential for practical applications.

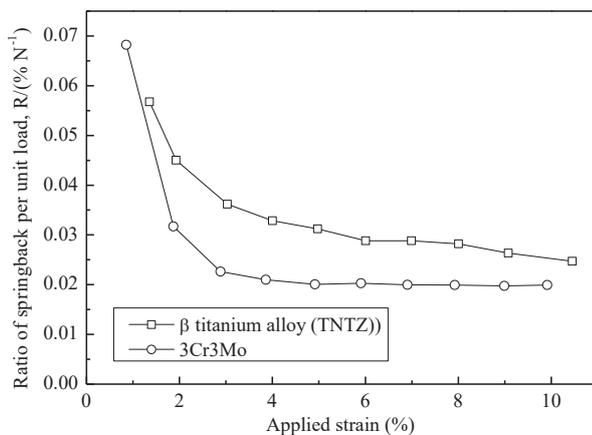


Fig. 2 Ratio of springback per unit load as a function of applied strain for 3Cr3MO and TNTZ, and strains for calculation of springback ratio (inset).

## References

- [1] K. Narita, M. Niinomi, M. Nakai, T. Akahori, H. Tsutsumi and K. Oribe, *Adv. Mater. Res.*, 89-91: 40 (2010).
- [2] N. Narushima. *J. Jpn. Biomater.*, 23: 86-94 (2005).
- [3] X.L. Zhao, M. Niinomi, M. Nakai, T. Ishimoto and T. Nakano, *Mater. Sci. Eng. C*, 31:1436 -1444 (2011).
- [4] H. Matsumoto, K. Kodaira, A. Chiba. *J. Jpn. Inst. Metals.*, 72: 989-996 (2008).
- [5] H. Matsumoto, S. Watanabe, S. Hanada. *Mater. Sci. Eng. A*, 448(1-2): 39-48 (2007).

## Key Words

Titanium alloys, deformation-induced, spring back

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## Interstitial diffusion in a tetrahedrally close packed structure: oxygen diffusion in $\beta$ -tungsten

The diffusivity of interstitial atoms in complex structures has received scant attention and very little is known experimentally. Here, the particular case of interstitial oxygen in tungsten is considered, both for tungsten in the usual bcc structure and in the A15 structure.

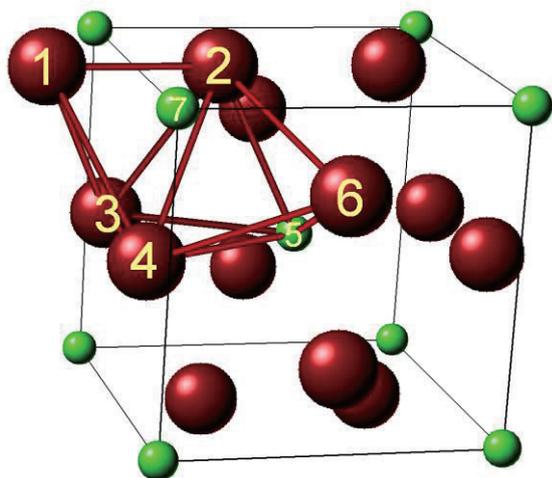


Figure 1 A15 structure, small green (large red) spheres represent 12 (14) - fold coordinated atoms. Tetrahedra are formed by atoms labeled 1,2,3,4; 2,3,4,5; 2,4,5,6 and triangles which bisect triangular bipyramids are formed by atoms labeled 2,3,4; 2,4,5; 3,4,5; and 2,4,6. Note that no interstitial atoms have been displayed.

Achieving metallic materials with good properties almost always involves processes in which diffusion plays an essential role. In recent years modelling diffusion in the most commonly observed simple structures, such as dilute solid solutions with fcc and bcc crystal structures, has been quite successful [1]. Generally, starting from ab initio electronic density functional methods a fair agreement with experimental data can be achieved. Even the presence of dislocations and other structural imperfections has been modelled with apparent success [2]. Diffusion in complex crystal structures is still rather poorly understood because there are many possible mechanisms through which diffusion can occur. Here, we consider the simplest complex structure, the so-called A15 structure which occurs for compounds such as  $\text{Cr}_3\text{Si}$  and also for W when a few percent of interstitial N, O or F is dissolved. We select this particular structure because it is the simplest representative from the class of tetrahedrally close packed structures which features in many intermetallic compounds. A particularity of this class of structures is that tetrahedra between nearest neighbor atoms entirely fill the whole crystal volume.

Therefore, in spite of the structural complexity, the candidate locations for sufficiently large interstitial atoms is easily guessed to be either the centers of these tetrahedra or the centers of the triangles where two tetrahedra touch one another. In the A15 structure there are just 3 crystallographically distinct tetrahedra and just 4 distinct triangular bi-pyramids, see figure 1. Thus there are just 7 likely positions for interstitial species. Closer examination by means of ab initio electronic density functional calculations of these 7 positions revealed that for interstitial oxygen in tungsten with the A15 structure, so-called  $\beta$ -W, there are just two energy minima among the 7 candidate positions: the center of tetrahedron 2,3,4,5 is a local energy minimum about 0.75 eV above the global energy minimum at the center of triangle 2,4,6; while the other positions are either saddlepoint configurations (1,2,3,4 and 2,4,5) or not being associated with energy extrema at all (2,4,5,6; 2,3,4; 3,4,5). Furthermore, when these positions are connected, it is easy to show that there are only three pathways which give rise to diffusion through the crystal. These three pathways can be represented as sequences of centers of triangles and tetrahedra as follows:

sequence a:  $2,3,4,5 \leftrightarrow 2,4,5 \leftrightarrow 2,4,5,6 \leftrightarrow 2,4,6$

sequence b:  $2,3,4,5 \leftrightarrow 3,4,5 \leftrightarrow 3,4,5,6$

sequence c:  $2,3,4,5 \leftrightarrow 2,3,4 \leftrightarrow 1,2,3,4 \leftrightarrow 1,2,4 \leftrightarrow 1,2,4,7$

where the sequence can be followed in both directions. All interstitial diffusion pathways will consist of sequences a and/or b and/or c. In figure 2 the minimum energy paths for the three sequences are shown. It is immediately evident that the lowest energy barrier of about 1.14 eV occurs for sequence a. Long-ranged atomic transport of interstitial O in  $\beta$ -W is thus possible with an activation energy of just 1.14 eV, as sequences b and c are not required. This energy barrier is of the same magnitude as diffusion activation energies for normal metals (read non-transition metals) in an fcc Al matrix. However it is much higher than the activation energy for interstitial O diffusion in bcc W. In bcc W interstitial O occupies the tetrahedral position. O can move from one bcc tetrahedral interstice to another with an intermediate saddlepoint configuration occurring on the (110) plane. The activation energy barrier is just 0.17 eV. Ignoring the diffusivity prefactor, it follows that interstitial O can diffuse much faster in bcc-W than in  $\beta$ -W. However, when the O concentration exceeds a threshold of 7 atomic percent, bcc-W undergoes a phase transformation to  $\beta$ -W as was recently shown in another study [3]. Therefore, once the phase transformation to  $\beta$ -W occurs, the interstitial O gets trapped, which explains the remarkable stability of  $\beta$ -W, such as in the

case of  $\beta$ -W nanowires which are stable to quite high temperatures [4,5].

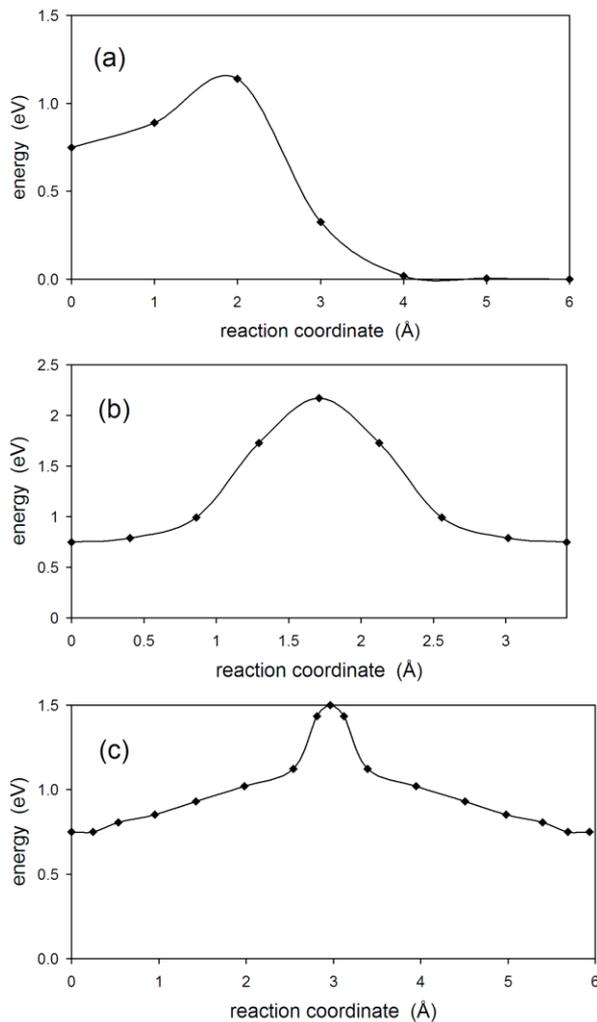


Figure 2 Minimum energy pathways for interstitial oxygen diffusion in  $\beta$ -W according to sequences a, b, and c. Energies are relative to the energy at the center of triangle 2,4,6, the most stable position for an oxygen interstitial in  $\beta$ -W.

As a more general conclusion we find that complex structures provide a range of interstitial positions, some of which are likely to be much more favorable than others. Therefore notable traps for diffusing species are likely to exist. This means that quite generally we can expect diffusivities of interstitial species in complex structures to be rather low in comparison to simpler crystal structures such as bcc and fcc. Diffusion of interstitials into complex phases is thus also likely to be slow which makes that they might not generally provide good sinks or getters, except perhaps at the interface between complex phase precipitates and the bcc/fcc matrix. On the other hand, when interstitials promote the phase transformation towards the complex phase, it is possible that the reverse transformation of complex phase to bcc/fcc phase is slowed down by the tardy process of getting the interstitials out of the complex phase.

## References

- [1] D. Simonovic and M.H.F. Sluiter, Phys. Rev. B **79**, 054304 (2009).
- [2] A. Ishii, S. Ogata, H. Kimizuka, and Ju Li, Phys Rev. B **85**, 064303 (2012).
- [3] M.H.F. Sluiter, Phys. Rev. B **80**, 220102R (2009).
- [4] T. Karabacak, P.-I. Wang, G.-C. Wang, T.-M. Lu, Thin Solid Films **493**, 293 (2005).
- [5] K.L. Klein, S.J. Randolph, J.D. Fowlkes, L.F. Allard, H.M. Meyer III, M.L. Simpson, P.D. Rack, Nanotechnology **19**, 345705 (2008).

## Key Words

diffusivity, tetrahedrally close packed, interstitial, tungsten, oxygen

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## Title: Exploration of lead-free ferroelectric/piezoelectric ceramics from first-principles

### Introduction:

In this project Beckman and Nishimatsu studied the lead-free perovskite compounds  $\text{KNbO}_3$  (KNO) and  $\text{BaTiO}_3$  (BTO). During the first part of the project the structural, elastic, and piezoelectric behavior of KNO was studied using *ab initio* first principles methods. For the first time in the literature, the full tensors were reported for all known phases. During the second part of the project the electrocaloric response of BTO was calculated using the FERAM software package developed by Nishimatsu. This is the first time that the electrocaloric response has been calculated using this type of theoretical method.

### Body:

The elastic and dielectric properties of the four experimentally known phases of  $\text{KNbO}_3$  (KNO) are investigated by first-principles methods and reported in Ref. [1]. The atomic structure and atomic pair distribution functions are reported and confirm the established hypothesis that the covalent hybridized bonds between the Nb and O atoms are responsible for the ferroelectricity in KNO. In addition, the Born effective charge tensor is calculated to reveal the relation between Nb–O bonds hybridization and ferroelectric structural distortion. The dielectric, elastic, and piezoelectric properties of each phase are presented and compared to experimental measurements in the literature. The computed structures are found to match experiment to an accuracy of approximately 2%. Although there have been very few experimental studies of single crystal KNO, it is found that the elastic parameters computed for orthorhombic KNO agree with the measured values to better than 25%, which is within the anticipated exchange-correlation error; however, the computed piezoelectric coefficient differ from the experimental values by as much as 50%, which suggests that the disagreement may not be solely due to the theoretical approximations and in fact the experimental results should be readdressed.

The perovskite crystal  $\text{BaTiO}_3$  (BTO) is modeled using the first-principles based effective Hamiltonian developed by Nishimatsu in the FERAM software package. These simulations are performed to estimate the pyroelectric response in the ferroelectric crystal. The electrocaloric temperature change,  $\Delta T$ , is calculated for different temperatures and externally applied electric fields.

The electrocaloric effect (ECE), studied here, is important because it holds promise for application in future solid-state refrigeration technology. Domestic refrigeration for food storage is a major consumer of energy. The US Energy Information

Administration (EIA) reported that in 2005 26.7% of household electricity is used in the kitchen and that of this 64% goes toward cooling food. These numbers suggest that 17.1% of US domestic electrical energy is used for food storage. It is approximated that the US has around 37 power plants dedicated to producing energy for domestic refrigeration.

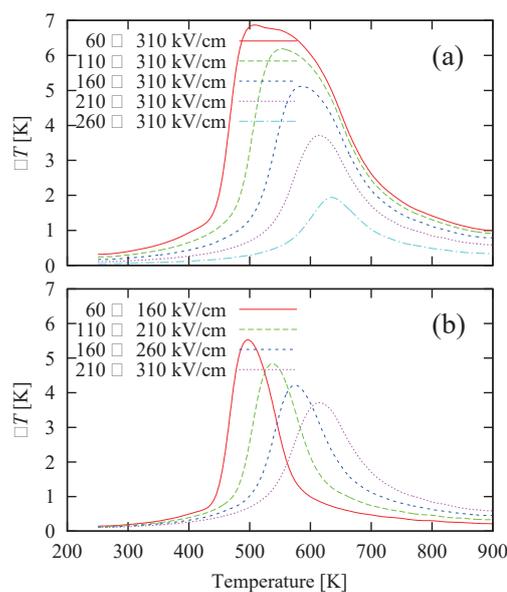


Fig. 1 The electrocaloric response of BTO as predicted by Beckman and Nishimatsu.

Refrigerators are relatively low efficiency devices that require a large mechanical condenser to compress a gas. Moving to solid-state cooling has the potential to dramatically increase the efficiency of refrigeration devices because it is based on changing the local structure (order) of atoms in a crystal by directly applying an electric field to the crystal. Because so much energy is used for refrigeration, even a modest increase in efficiency would result in a dramatic savings, for example increasing efficiency by 2.7% is enough to conserve one power plant worth of energy.

The results from this study predict that BTO is indeed a reasonable electrocaloric material and more importantly it is demonstrated that this computational approach can be used to predict the magnitude of the ECE in new material systems. The calculated electrocaloric temperature change is found to be as large as 5-6 K can be achieved for a relatively small electric field gradient, less than 100 kV/cm, if the applied fields have a small absolute magnitude. These results are counter to the current trend in research where

scientists and engineers are examining materials that require large field gradients. These results have been submitted for publication and are under review in Ref. [2].

**References:**

[1] L. F. Wan, T. Nishimatsu, and S. P. Beckman, "*The structural, dielectric, elastic, and piezoelectric properties of  $\text{KNbO}_3$  from first-principles methods,*" J. Appl. Phys. **111**, 104107 (2012).

[2] S. P. Beckman, L. F. Wan, Jordan A. Barr, and T. Nishimatsu, "Effective Hamiltonian Methods for Predicting the Electrocaloric Behavior of  $\text{BaTiO}_3$ ," under review at Mater. Lett. (2012).

**Key Words:**

Perovskite, Ferroelectric, Electrocaloric Effect, Effective Hamiltonian, FERAM

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Activity Report

# Integrated Projects



## FY2010-2011 Integrated Projects

No.	PI	Host	Proposed Research	Title	Affiliation	Term
10PJT1	Louis-Pierre Regnault	K. Ohoyama	Development of IMR Neutron Spectrometer for Novel Material Science in J-PARC	Head of Neutron Diffraction Lab.	ILL, France	FY2010-2011
10PJT2	Arndt Remhof	S. Orimo	Lithium Fast-Ion Conduction in Complex Hydrides	Group Leader	EPMA, Switzerland	FY2010-2011
10PJT3	Thierry Epicier	T. Konno	Structural and Chemical Analysis on Doped Ceramics by Transmission Electron Microscopy	Professor	INSA Lyon, France	FY2010-2011
10PJT4	Junichiro Kono	H. Nojiri	Development of a Compact Pulsed Magnet for high-Field Magneto-optical Studies of Carrier and Exciton Dynamics in Nanostructures	Professor	Rice University, USA	FY2010-2011

## Development of Neutron Spectrometer for Novel Material Science at J-PARC

*IMR neutron group is advancing a project to construct a new neutron spectrometer at J-PARC/MLF for future material science in Tohoku Univ. based on collaborations with faculties and institutes of Tohoku Univ., and KEK. This ICC-IMR project aimed at creating international collaborations which will develop into advanced material science using the Tohoku Univ. spectrometer in J-PARC. Based on discussions in international workshops and intervisitations supported by ICC-IMR, we succeeded in beginning international collaborations with leading scientists in neutron science, which shows the presence of IMR in neutron science to the world.*

Neutron scattering is an indispensable probe for advanced researches of material science because of its unique advantages: observation of spins and light atoms, and, observation of spatial and time correlations of spins and atoms. Tohoku University, in particular IMR, is a center of excellence on material science by neutron scattering based on long-established researches in JRR-3 and top facilities in the world. The Tohoku Univ. neutron group, centering on IMR, aims at constructing a new spectrometer at J-PARC/MLF as a future plan of advanced material science. Figure 1 shows a rendering image of the proposed spectrometer which will be constructed at J-PARC. The instrument, named POLANO (POLarisation Analyses Neutron spectrOmeter), is characterized by observations of spins and hydrogens using polarised neutrons. The construction of POLANO has already been authorized by J-PARC Center. Though the importance of polarised neutrons for advanced materials science is commonly understood, facilities in which polarised neutron scattering experiments can be performed are limited even in

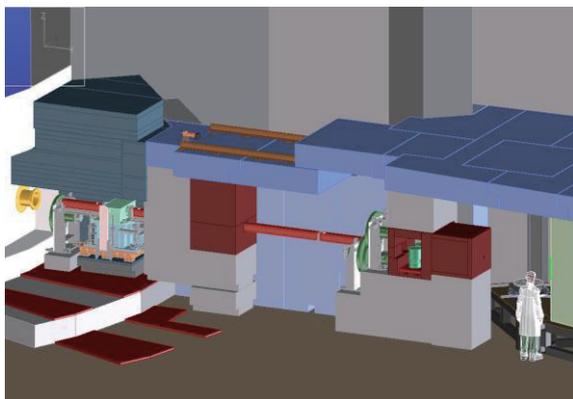


Fig.1 Rendering Image of Tohoku Univ J-PARC spectrometer, POLANO.

the world. Thus, POLANO will be used for international collaborative researches. This means that its design and concept should be discussed from global view points, to utilize this spectrometer in top material science in the world. Moreover, to develop ability of POLANO to the global level, it is definitely important to share experiences of leading scientists in the world. From these points, therefore, building of international collaborations for POLANO project is needed.

For this purpose, we obtained financial supports from ICC-IMR: 3.6M JPY in 2010FY and 2.1M JPY in 2011 FY, which were mainly used for organization of international workshops and intervisitations of scientists. During the two years term of this ICC-IMR project, we held two international workshops in IMR (Fig.2). One of the workshop, "Novel Material Science using Polarized Neutron -- Discussions for J-PARC Polarized Chopper Spectrometer Project by KEK-Tohoku Univ.", was held on 6~8-Jan-2011, which aimed at discussing roles and possibilities of polarised neutrons for future material science. The second workshop, "Novel Material Science by Neutron Scattering -Polarization Analysis & Cross-Correlation Method", was held on 18~19-NOV-2011, which aimed at discussing novel polarised neutron techniques to make technical breakthroughs. The second one was recognized as an official satellite meeting of 1<sup>st</sup> Asia-Oceania Conference on Neutron Scattering held in Tsukuba. For the workshops, we invited leading scientists of neutron facilities in the world: Dr. M. Hagen and Dr. M. Matsuda of Oak Ridge National Laboratory (USA), Dr. E. Lelievre-Berna of Institut Laue-Langevin (France), Dr. W.T. Lee of Bragg Institute (Australaria), Dr. S Rosenkrantz of Argonne National



Fig.2 One of the ICC-IMR workshops of this project held in IMR. Roles of polarised neutrons for advanced materials were discussed with leading scientists of neutron science.

Laboratory (USA), Prof. J.G. Park of Seoul National University, Dr. I Zaliznyak of Brookhaven National Laboratory (USA), Dr. W.C. Chen of National Institute of Standards and Technology (USA). With the experts in the world as well as in Japan, we could discuss roles of POLANO and IMR intensively. All the presentations in the two workshops were printed and distributed by the support of ICC-IMR. Note that, based on discussions in the workshops, a novel technique of neutron scattering, “modified cross correlation method”, has been proposed and published [1].

Intervisitations of scientists are another important aim of this ICC-IMR project. Some Japanese members of this ICC-IMR project visited Oak Ridge National Laboratory and Institut Laue-Langevin, and discussed with experts of polarised neutron experiments. Ohoyama, who was the principle person of this project, had seminars in Oak Ridge National Laboratory (USA) on Sep-2010 and Korea Atomic Energy Research Institute (Korea) in Nov-2011 to describe details of POLANO project and activity of IMR in neutron science. As one of concrete results, Center of neutron science for advanced materials of IMR has made collaboration arrangement with Center for Korean J-PARC Users.

In summary, by the support of ICC-IMR, we have obtained fruitful results about international collaborations. Firstly, we have succeeded in building up collaborations with many leading neutron scientists in the world and in Japan, which will be quite important for the construction of POLANO and novel material science. Secondly, by the organization of the international workshops, IMR has been recognized as one of the world center of material science using polarised neutrons. In fact, in a summary talk in one of the workshops, sustained workshops on polarised neutrons in IMR were required by Dr. Kakurai of JAEA.

## References

[1] K. Tomiyasu, M.Matsuura, H.Kimura, K.Iwasa, K.Ohoyama, T.Yokoo, S.Itoh, E. Kudoh, T.Sato, M.Fujita, Nucl. Instrum. Meth. Phys. Res. A **677** (2012) 89-93

## Key Words

Neutron scattering, spin dynamics, polarised neutron, hydrogen, J-PARC, international collaborations,

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## Lithium Fast-Ion Conduction in Complex Hydrides

Complex hydrides can be a potential candidate for solid electrolytes for lithium ion batteries. In this study, we investigated the electrical conductivities of complex hydrides  $\text{Li}_2\text{BNH}_6$  and  $\text{Li}_4\text{BN}_3\text{H}_{10}$  consisting of  $[\text{BH}_4]^-$  and  $[\text{NH}_2]^-$  anions, focusing on their low melting temperatures. We also studied the localized rotational diffusion of the  $[\text{BH}_4]^-$  anions in  $\text{LiBH}_4\text{-Li}$  system.

We have reported that complex hydrides  $\text{Li}_2\text{BNH}_6$  and  $\text{Li}_4\text{BN}_3\text{H}_{10}$  consisting of  $[\text{BH}_4]^-$  and  $[\text{NH}_2]^-$  complex anions, shown in Figure 1, exhibit lithium fast-ion conduction [1]. The relatively low melting temperatures (around 360 K and 460 K for  $\text{Li}_2\text{BNH}_6$  and  $\text{Li}_4\text{BN}_3\text{H}_{10}$ , respectively) suggest the possible enhancement of total ion conductivity in these temperature ranges. As shown in Figure 2,  $\text{Li}_2\text{BNH}_6$  exhibits fast-ionic conductivity of  $1 \times 10^{-4}$  S/cm even at room temperature, which is four and five orders of magnitude higher than those of the host hydrides  $\text{LiBH}_4$  and  $\text{LiNH}_2$ , respectively. Moreover, the conductivity increases monotonically upon heating. The activation energy for conduction decreases significantly at around 368 K from 0.66 eV (303–348 K) to 0.24 eV (above 368 K) as a result of the melting of  $\text{Li}_2\text{BNH}_6$ . The total ionic conductivity reaches  $6 \times 10^{-2}$  S/cm after melting at the highest temperature measured, 378 K.  $\text{Li}_4\text{BN}_3\text{H}_{10}$  also shows high conductivity of  $2 \times 10^{-4}$  S/cm at room temperature, and the value reaches  $2 \times 10^{-1}$  S/cm at 513 K after melting. Raman spectroscopy confirmed both the  $[\text{BH}_4]^-$  and  $[\text{NH}_2]^-$  complex anions remain intact within  $\text{Li}_2\text{BNH}_6$  and  $\text{Li}_4\text{BN}_3\text{H}_{10}$  even after melting. These results suggest that  $\text{Li}_2\text{BNH}_6$  and  $\text{Li}_4\text{BN}_3\text{H}_{10}$  could be used as a new type of “ionic liquid” as well as a solid-state fast-ionic conductor [2].

We also investigated the localized rotational diffusion of the  $[\text{BH}_4]^-$  complex anions in  $\text{Li}(\text{BH}_4)_{1-x}\text{I}_x$ , which shows lithium fast-ion conductivity of the order of  $10^{-5}$  S/cm at room temperature, by means of quasielastic and inelastic neutron scattering and Raman spectroscopy to clarify the mechanism of the increased ion conductivity [3, 4]. The motions of  $[\text{BH}_4]^-$  are thermally activated and characterized by activation energies in the order of 40 meV. The motion is dominated by 90 reorientations around the 4-fold symmetry axis of the tetrahedrally shaped  $[\text{BH}_4]^-$  ions. As compared to the pure  $\text{LiBH}_4$ , the presence of  $\text{I}^-$  markedly reduces activation energies and increases the rotational frequencies by more than a factor of 100. The result suggests that the rotational motion of the translationally static  $[\text{BH}_4]^-$  anions may enhance the mobility of  $\text{Li}^+$  ions (paddle wheel mechanism).

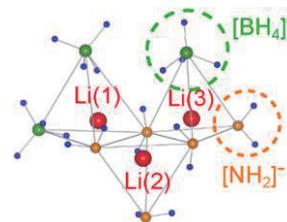


Fig. 1 Local atomistic structure of the complex hydride  $\text{Li}_4\text{BN}_3\text{H}_{10}$ .  $\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$  have plural occupation sites for  $\text{Li}^+$  ions with different tetrahedral coordination consisting of  $[\text{BH}_4]^-$  and  $[\text{NH}_2]^-$  anions

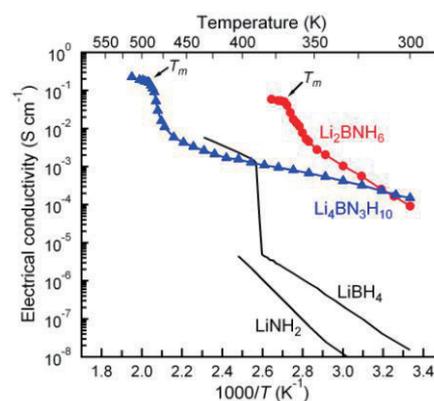


Fig. 2 Electrical conductivities of  $\text{Li}_2\text{BNH}_6$  and  $\text{Li}_4\text{BN}_3\text{H}_{10}$ . The melting temperatures are indicated as  $T_m$ . For reference, the data of the host hydrides  $\text{LiBH}_4$  and  $\text{LiNH}_2$  are also shown.

### References

- [1] M. Matsuo, A. Remhof, P. Martelli, R. Caputo, M. Ernst, Y. Miura, T. Sato, H. Oguchi, H. Maekawa, H. Takamura, A. Borgschulte, A. Züttel and S. Orimo, *J. Am. Chem. Soc.* 131, 16389 (2009).
- [2] Y. Zhou, M. Matsuo, Y. Miura, H. Takamura, H. Maekawa, A. Remhof, A. Borgschulte, A. Züttel, T. Otomo and S. Orimo, *Mater. Trans.* 52, 654 (2011).
- [3] P. Martelli, A. Remhof, A. Borgschulte, R. Ackermann, T. Strässle, J.P. Embs, M. Ernst, M. Matsuo, S. Orimo and A. Züttel, *J. Phys. Chem. A* 115, 5329 (2011).
- [4] A. Borgschulte, R. Gremaud, S. Kato, N.P. Stadie, A. Remhof, A. Züttel, M. Matsuo and S. Orimo, *Appl. Phys. Lett.* 97, 031916 (2010).

### Key Words

complex hydride, fast-ion conduction, ionic liquid

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## Structural and chemical analysis on doped ceramics by transmission electron microscopy

*In complex oxides, metallic and oxygen atoms occupy several crystallographically non-equivalent sites, on which the electronic states of the impurities are strongly sensitive. By employing wave-front reconstruction techniques on high-resolution TEM images taken under Cs-corrected conditions and Z-contrasts in atomically resolved STEM, we can directly clarify the favorable sites for dopant atoms.*

Understanding the optical properties of materials requires a detailed investigation of their microstructure, especially regarding the exact location of the required dopants (e.g. rare earth elements such as  $\text{Ce}^{3+}$ ,  $\text{Nd}^{3+}$  or  $\text{Yb}^{3+}$ ). For example, it was recently shown by careful Transmission Electron Microscopy (TEM) observations that Ce strongly segregates at grain-boundaries within YAG (Yttrium Aluminium Garnet  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ) [1].

The oxide materials to be investigated in the current proposal includes YAG (yttrium-aluminum garnet) doped with RE (rare-earth), such as cerium or ytterbium, prepared either in a single or polycrystalline form in INSA-Lyon. We use FEI Titan 80-300 (S)TEM installed in Tohoku University as a major characterization tool (Fig.1), and the images taken will be analyzed quantitatively with a help of several simulation techniques, including the one developed in INSA-Lyon.

We have performed both High Resolution (HR) and HAADF imaging on pure YAG and Yb-doped YAG polycrystals, using a TITAN FEI electron microscope, operating at 300 kV. On the one hand, this instrument is equipped with a  $C_s$  aberration corrector on the objective lens, allowing a resolution down to 0.1 nm to be obtained in the HREM mode[2]. On the other hand, it is also equipped with an annular detector collecting electrons in a 70-210 mRad angular range. Nanoprobe chemical analysis was also simultaneously performed using an EDAX EDX



Fig. 1 Cs corrector at the objective lens, which makes the resolution of phase contrast image better than 0.1 nm.

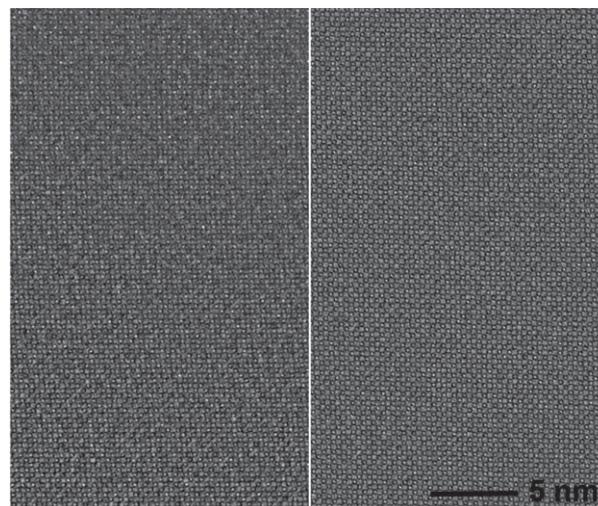


Fig. 2 HAADF-STEM images of two regions of similar thicknesses (as attested by low-loss EELS spectra) from a 1.4 at. % Yb-doped sample (left) and a pure YAG sample (right).

(Energy-Dispersive X-ray) analyser mounted on the microscope.

Whereas Cs-corrected HREM failed to reveal the distribution of Yb-containing atomic columns, the STEM-HAADF imaging mode appeared to be more efficient owing to its sensitivity to Z. Figure 1 shows a comparison of a 1.4 at.%Yb-doped and a pure YAG samples when observed along the [001] azimuth. A high density of brighter columns is observed for the doped material, which can be consistently analysed in terms of statistics as imaging Yb-containing atomic columns. Dedicated HAADF-STEM image simulations confirm this finding. This work shows that no segregation, neither clustering of Yb ions occurs in polycrystalline YAG.

To summarize, we have demonstrated that dopant distribution in oxide materials can be performed with aberration corrected scanning transmission electron microscopy.

### References

- [1] W. Zhao, C. Mancini, D. Amans, G. Boulon, T. Epicier, Y. Min, H. Yagi, T. Yanagitani, T. Yanagida, A. Yoshikawa *Jpn. J. Appl. Physics* 49 (2010) 022602
- [2] K Sato, T.J. Konno, Y. Hirotsu, , *J. Appl. Phys.* **107** (2010) 024304.

### Key Words

Optical ceramics, Yb-doped YAG, atomic STEM-HAADF

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## Development of a Compact Pulsed Magnet for High-Field Magneto-optical Studies of Carrier and Exciton Dynamics in Nanostructures

*We have developed a table-top pulsed magnet system for time-resolved magneto-optical spectroscopy studies, including time-domain terahertz spectroscopy measurements of cyclotron resonance. Magnetic fields as high as 30 T have been generated by using a compact capacitor bank together with a miniature pulsed coil cooled in a cryostat. The system allows direct optical access through an optical window with a large numerical aperture, ideal for ultrafast and nonlinear optical studies in a high magnetic field.*

The purpose of this research is to develop a table-top pulsed magnet system that can be combined with conventional ultrafast optical spectroscopy methods for the study of dynamics of high-density carriers and excitons in low-dimensional systems in quantizing magnetic fields. Such a system will open up new possibilities for investigating quantum coherence and correlations in condensed matter systems in the magnetic quantum limit with unprecedented time resolution.

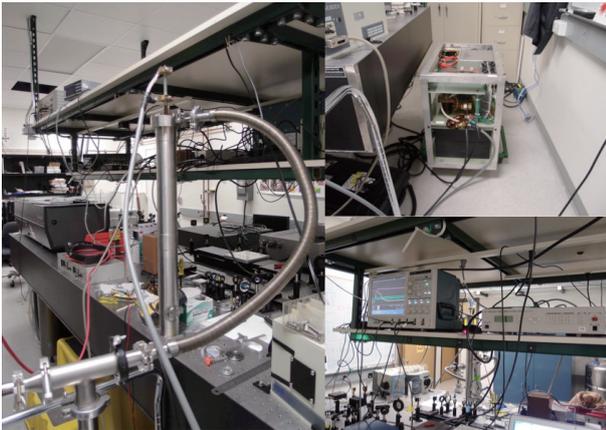


Fig. 1 Table top pulsed magnet system installed on the optical bench of the THz-spectroscopy. Cryostat(left), capacitor bank(right upper) and optics(right lower).

Figure 1 shows a photograph of the system developed at Rice University, Houston, Texas, USA. The system consists of a portable capacitor bank, a cryostat, and a miniature magnet. The cryostat has a horizontal free access bore of about 10.4 mm diameter at liquid nitrogen temperature. The sample is mounted on a cold finger made of a sapphire tube and cooling is made by a separate conventional helium-flow cryostat for optical microscopic spectroscopy. The two cryostats are joined together by a flexible joint sharing the isolation vacuum, and the total optical path is about 12 cm. This short distance is advantageous in performing ultrafast and nonlinear laser spectroscopy experiments. Use of fiber optics is common in spectroscopic studies in high magnetic fields, but it deteriorates

time resolution by elongating short light pulses through finite dispersion. Our system avoids this problem by using free space optics with direct access to the sample via a window.

The specs of the capacitor bank are 5.6 mF capacitance and 2 kV charging voltage with a total energy of 11.2 kJ. Figure 2 shows the waveforms of the generated pulsed field at different charging voltages. The raising time is about 2 msec, and the total pulse width is about 10 msec. A magnetic field of 30 T is generated at 1800 V charging voltage; the current is 5.2 kA at 30 T, and the interval of successive pulse is about 5 minutes. We have not found any interference with the spectroscopy setup, and the effect of the leakage field was not detected.

While a number of groups and laboratories in the world have expertise in ultrafast optics and pulsed high magnetic fields separately, no facilities currently exist which combine the two. National high magnetic field facilities in different countries have some limited capabilities of performing time-resolved optical experiments, but fields used in such experiments are DC fields, which naturally limit the highest field available. Our system will allow us to investigate an entirely new class of phenomena in the magnetic quantum limit with a unique table-top environment in a university laboratory setting.

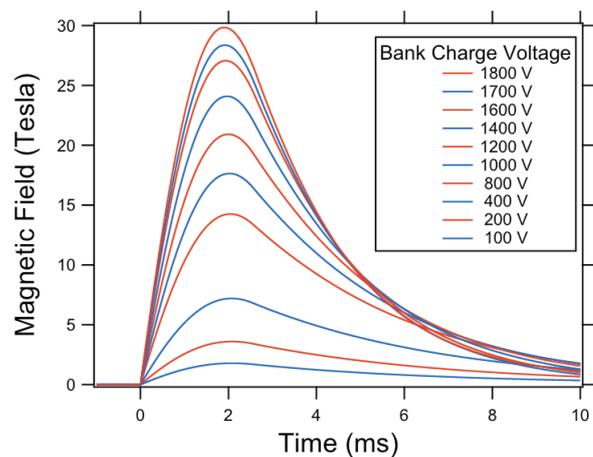


Fig. 2 Waveform of pulsed magnetic fields at different charging voltages of the capacitor bank.

### Key Words

High Magnetic Fields, Ultrafast and Nonlinear Optical Spectroscopy, High-Field Magneto-optics

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Activity Report

Workshops



## FY 2011 Workshops

No.	Chairperson	Title of Workshop	Place	Date
11WS1	K. Takanashi	5th International Workshop on Spin Currents	Sendai International Center	2011.7.25-7.28
11WS2	M. Fujita	Search for new Physics in Transition Metal Compound by Spectroscopies	IMR Lecture Hall	2011.7.28-7.30
11WS3	T. Goto	The 6th International Workshop on Nano, Bio and Amorphous Materials	Zao, Miyagi	2011.8.8-8.9
11WS4	Y. Kawazoe	The 6th General Meeting of ACCMS-VO	IMR Lecture Hall	2012.2.10-2.12

## Search for new physics in transition metal compounds by spectroscopies

*The novel physics generated by the electronic correlation and the orbital degree of freedom in transition metal compounds was intensively discussed in this workshop. The importance of the material research and the spectroscopy such as neutron, X-ray, Raman, photoemission, STM/STS, NMR, and  $\mu$ SR, were also addressed for the study of the exotic electronic states in the real, momentum and energy spaces.*

The international workshop "Recent Progress on Spectroscopies and High- $T_c$  Superconductors" was held on July 28<sup>th</sup>-30<sup>th</sup>, 2011 in the Lecture Hall of Institute for Materials Research (IMR), Tohoku University. This workshop aimed to discuss novel physics generated by the electronic correlation and the orbital degree of freedom in transition metal compounds. Recently, the multi-orbitals character has been realized in newly discovered iron-based superconductors for the understanding of their electronic states. Furthermore, the orbital degeneracy is recognized to play a crucial role in the mechanism of giant thermoelectric power in carrier doped cobalt oxides. These issues related orbitals are important to be studied from a microscopic way to understand their novel physics. Therefore, we selected the following topics as the main target of discussion.

- 1: High- $T_c$  superconductivity in transition metal compounds
- 2: Giant thermoelectric power in cobalt oxide
- 3: Magnon Hall effect in vanadium oxide
- 4: Advanced spectroscopic techniques.



Fig. 1. A picture of workshop. 90 researchers including many young scientists participated in the workshop and exchanged the information.

There were 35 oral presentations (29 experimental and 6 theoretical works) and ~90 researchers participated in the workshop. We invited 8 outstanding speakers from abroad, who introduced many new results and overviews on superconductors. The research results in the above exciting fields were discussed to share what are the important and fundamental issues to be solved by spectroscopies. The complementary use of quantum beam spectroscopies was also discussed. The participants actively discussed and exchanged the information during the workshop, and we confirmed the pivotal contribution of spectroscopy to the orbital-related physics. We note that the opening of this workshop at a relatively early stage after the big earthquake, which was occurred on March 2011, was a very good opportunity to show our activity in Tohoku University to our research fields. The workshop has actually received favorable impressions and opinions. We would like to thank all participants for their active contributions in the workshop, and the support from ICC-IMR.

### Key Words

Quantum Beam spectroscopy, J-PARC, SPring-8, Orbital physics, Strongly correlate electron system

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Fig. 1. A picture of get together party.

## The 6<sup>th</sup> International Workshop on Nano-, Bio- and Amorphous Materials

*Research on biomaterials has recently become crucial due to strong demands in developing materials for replacing human-body parts. The international workshop on nano-, bio- and amorphous materials has provided a valuable forum for presentation, discussion, idea sharing, collaboration as well as interdisciplinary exchanges among the experts, researchers and students from different fields and expertises to meet and establish the interface science on biomaterials.*

The 6th International Workshop on Nano-, Bio- and Amorphous Materials was held on August 8 – 9, 2011 in Miyagi-Zao Royal Hotel, Miyagi, Japan as the last series of international forums in the frame of a 5-year research and collaboration project on the Interface Science of High Functional Biomaterials. The project involves 3 institutions, namely Institute for Materials Research, Graduate School of Dentistry (both are of Tohoku University) and Research Institute for Applied Mechanics, Kyushu University. The Workshop was organized under the financial supports from:

- Highly-functional Interface Science: Innovation of Biomaterials with Highly functional Interface to Host and Parasite (MEXT),
- International Collaboration Center (ICC-IMR), Tohoku Univ.
- Global COE Program: Materials Integration International Center of Education and Research, Tohoku University.

The Workshop was held in a two-day technical program in which 22 papers were presented including 3 invited lectures by researchers of bio-/medical materials from the People Republic of China. About 50 participants consisting of experts, researchers and students attended the Workshop. The invited speakers in this workshop were Dr. Guangyin Yuan (School of Materials Science, Shanghai Jiao Tong University), Dr. Yu-Feng Zheng (Dept. of Advanced Materials and Nanotechnology, Beijing University) and Dr. Cuanliang Feng (State Key Lab. Metal Matrix Composites, Shanghai Jiao Tong University).



Fig. 1. Participants of the 6th International Workshop on Nano-, Bio- and Amorphous Materials in a photo session.

The lecture by Dr. G.Y. Yuan was on the research on Mg alloy as a degradable cardiovascular stent material. The talk described the fabrication of cardiovascular stent prototype from the so-called JDBM alloy which exhibits outstanding mechanical properties, excellent corrosion resistance and biocompatibility. Dr. Y.F. Zheng presented the study on bulk metallic glasses for biomedical application. Meanwhile, Dr. C.L. Feng's lecture was on the investigation of cell adhesion on nano-patterned polymeric fabricated by reactive microcontact printing. Besides the invited lectures, numbers of papers on bio, dental and skeletal as well as amorphous and nanostructured materials were presented by researchers and students.



Fig. 2. A situation during Japanese-style banquet in the 6th International Workshop on Nano-, Bio- and Amorphous Materials

The different academic backgrounds among the participants has provided the interdisciplinary exchange and enriched the viewpoints during the discussion of a specific topic. In addition, this workshop also accommodated researchers to have a good opportunity and forum to present their research in English as well as to touch the cutting edges of the development on bio, nanostructured and amorphous materials. Finally, in the closing remarks, Prof. Takashi Goto as one of organizers emphasized the importance of continuation for the project on the interface science of biomaterials as a means and place to develop collaboration among interdisciplinary field and studies.

### Key Words

International forum, biomaterials, interdisciplinary collaboration

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## Highlight of ICC-IMR International Workshop The 6<sup>th</sup> General Meeting of Asian Consortium on Computational Materials Science – Virtual Organization (ACCMS-VO) February. 10-12, 2012, Chairperson Y. KAWAZOE (IMR)

*This is the 6<sup>th</sup> annual meeting of “off the net” of the virtual organization for computational materials scientists mainly in the Asian region, who are working collaboratively daily via international computer network using our supercomputer at the Center for Computational Material Science, Institute for Materials Research, Tohoku University (CCMS, IMR, TU). The ACCMS started in Sendai with only 16 researchers from Japan, China, India, Russia, Thai, Iran, US, and Canada in August 2000. After this meeting, 6 main meetings in India, Russia, China, Korea, Vietnam, and Singapore, 6 VO meetings, and 3 WG meetings in Sendai, Singapore, and Korea were held. Especially VO meetings have been held in Sendai continuously every fiscal year. We have published the Proceedings for all the main meeting including invited talks and some of the oral talks from international journal publishers. The present meeting focuses on designing efficient hydrogen storage materials and new methodologies in computational materials science, using the supercomputer at IMR and other member institutions aiming to use the Computer K in Kobe. About 120 researchers from 13 countries gathered supported by ICC-IMR and other organizations, and not only present their recent research results and exchange ideas but also mixed up to start new collaborations among them. These new international collaborations will be continued on the computer network to establish ACCMS-VO as a research basis of the members. The details of the meeting and activities are open through our ACCMS webpage; please check <http://www-lab.imr.tohoku.ac.jp/~accmsvo6/>.*

*In order to hold Asian Consortium on Computational Materials Science (ACCMS) general/working group/virtual organization (VO) meetings periodically, and more effectively and smoothly, representatives of the participants from China, India, Japan, Korea, Taiwan, Thailand, Russia, and Singapore had a meeting during ACCMS-VO6 meeting. Then, we decided that IMR of Tohoku University will continue to host ACCMS-VO and the next one will be in autumn of 2012.*

The list of invited talks is shown below, which covers the recent important area in computational materials science and technology.

- I-1: Sukit Limpijumng (Suranaree University of Technology), “First Principles Study of Al Doped ZnO”
- I-2: Michael Ronald Philpott (University of California Berkeley), “Chymera Magnetic States of Graphene Nanodots”
- I-3: Kombiah Iyakutti (Noorul Islam University), “Investigation of Effect of Unequal Effective Mass Fermions in Graphene”
- I-4: Jian-Tao Wang (Chinese Academy of Sciences), “Mechanism for Direct Conversion of Graphite to Diamond”
- I-5: Gour P. Das (Indian Association for the Cultivation of Science), “Graphene-like Materials and Their Functionalization: Advent of a New Family”
- I-6: Umesh Waghmare (Jawaharlal Nehru Centre for Advanced Scientific Research), “Theory of Defects in Graphene and Related Nano-materials”
- I-7: Vijay Kumar (Dr. Vijay Kumar Foundation), “From Silicon Fullerenes to Bulk Metallic Glasses - My Golden Time with IMR”
- I-8: Kaoru Ohno (Yokohama National University), “All-electron Mixed Basis Approach for Accurate First Principles Calculations”
- I-9: Marcel Sluiter (Delft University of Technology), “Multinary Cluster Expansions for Dilute Al-Mg-Si and Al-Mg-Li Alloys”
- I-10: Yuan Ping Feng (National University of Singapore), “Spin-dependent Transport of GMR and TMR Devices”
- I-11: Katsumi Tanigaki (Tohoku University), “Charge Transfer to Organic Semiconductors on the Au Electrodes Modified by Self-assembled Monolayers: Comparison between Experiment and Theory”
- I-12: Momoji Kubo (Tohoku University), “Tight-Binding Quantum Chemical Molecular Dynamics Simulation on Tribochemical Reaction Dynamics of Diamond-Like Carbon”
- I-13: Kohzo Ito (University of Tokyo), “New Entropic Elasticity of Topological Network: Slide-Ring Materials”
- I-14: Masanori Tachikawa (Yokohama City University), “First-principles Calculations for Positron-attached Molecules”

I-15: Akira Terasaki (Kyushu University), "Advanced Spectroscopic Studies of Size-Selected Free Metal Clusters"

I-16: Vladimir R. Belosludov (Russian Academy of Science), "Equation of State and Effect of Self-preservation of Hydrogen Hydrate"

I-17: Jer-Lai Kuo (Academia Sinica), "Water on GaN Surfaces"

I-18: Fabio Pichierri (Tohoku University), "Theory of van der Waals Forces"

I-19: Kwang-Ryeol Lee (Korea Institute of Science and Technology), "Reactive MD Simulation of Si NW Oxidation"

I-20: Bing-Joe Hwang (National Taiwan University of Science and Technology), "A Combined Computational/Experimental Study on Pt-based Bimetallic Alloys for H<sub>2</sub>O<sub>2</sub> Oxidation Reaction"

I-21: Leslie Victor Woodcock (Kyonggi University), "High Performance Computing in the Theory of Liquids"

I-22: Jisoon Ihm (Seoul National University), "Scattering of Electronic Waves at Various Graphene Edges"



Activity Report

KINKEN WAKATE



## FY 2011 KINKEN WAKATE

No.	Chairperson	Title of Workshop	Place	Date
11Wakate	T. Goto	8th Materials Science School for Young Scientists (KINKEN WAKATE 2011)	Sendai	2011.12.1-12.2

## KINKEN WAKATE 2011 in conjunction with International Symposium of Global COE: Materials Integration and ASPT2011

*International Symposium of Global COE "Materials Integration" in conjunction with the 2nd International Symposium on Advanced Synthesis and Processing Technology for Materials (ASPT2011) and KINKEN WAKATE 2011 was held in Sendai on December 1-2, 2011. 40 scientists based overseas (including four invited lecturers) got together at the symposium with 125 researchers from Tohoku University (including 90 students) and 16 other guests and enjoyed enthusiastic discussion over most advanced subjects in the field.*

Global COE for "materials integration" held its last international symposium. To mark the end of the five-year program sponsored by the Ministry of Education, Culture, Sports, Science and Technology, the symposium was held in conjunction with the 2nd International Symposium on Advanced Synthesis and Processing Technology for Materials (ASPT2011) and KINKENWAKATE 2011: 8th Materials Science School for Young Scientists. The attendees were enjoyed enthusiastic discussion over most advanced subjects in the field. Many researchers of our GCOE had a chance to share their latest research results with the world's top materials scientists through oral and poster presentations. The program is as follows:

### Thursday, 1 December 2011

08:30-09:00 Registration

09:00-09:10 Opening ceremony

Opening address by chair of symposium and KINKEN WAKATE 2011, Prof. T. Goto (Tohoku Univ., Japan)

Opening address by co-organizer of ASPT2011, Prof. Z.Y. Fu (Wuhan Univ. Technol., China)

09:10-09:50 Keynote lecture 1

"Spark plasma sintering activities in Europe during the 2000's: a review", Prof. Mats Nygren (Stockholm Univ., Sweden)

09:50-10:30 Keynote lecture 2

"Probing nanoscale surfaces and interfaces – the scientific opportunities and challenges", Prof. Jian-Min Zuo (Univ. Illinois Urbana-Champaign, USA)

10:50-11:30 Keynote lecture 3

"The role of hydrogen in energy storage", Prof. Dr. Andreas ZÜTTEL (EMPA, Switzerland)

11:30-12:10 Keynote lecture 4

"Racetrack memory: the motion of domain walls in response to spin currents", Dr. Stuart S.P. Parkin, (IBM Almaden Research Center, San Jose, USA)

14:00-16:00 Concurrent sessions

16:00-16:20 Coffee Break

16:20-18:00 Concurrent sessions

18:00-18:30 Break

18:30- Banquet

### Friday, 2 December 2011

09:00-10:20 Concurrent sessions

10:20-10:40 Coffee Break

10:40-12:00 Concurrent sessions

12:00-13:30 Lunch

12:30-13:30 Poster Session

13:30-14:50 Concurrent sessions

14:50-15:10 Coffee Break

15:10-16:30 Concurrent sessions

16:30-17:30 Poster Session

17:30-18:00 Award Ceremony for Best Presentations

We appreciate all participants for their contributions leading great success of this symposium

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Fig. 1: Group photograph



Fig. 2: Poster presentation

Activity Report

# Short-term Visiting Researchers



## FY 2011 Short-term Visiting Researchers

Application No.	Name	Host	Proposed Research	Title	Affiliation	Term
11SV1	Chuanbin Wang	T. Goto	Lead-free New Ferroelectric Barium Titanate (BaTi2O5) : Application for Piezoelectric Actuator of Single Crystal Growth	Professor	Wuhan University of Technology	2011.8.7-8.20 2011.11.26-12.10
11SV2	Seyed Akbar Jafari	K. Yamada	Neutron Scattering Study of Collective Triplet Excitations in Graphene Based Systems	Assoc. Professor	Sharif University of Technology, Tehran, Iran	2011.8.1-8.15
11SV3	Atsufumi Hirohata	K. Takanashi	Experimental Demonstration of Persistent Current	Lecturer	University of York, UK	2011.8.20-9.4 2012.2.17-2.26
11SV4	Keivan Esfarjani	S. Awaji	Ab initio Calculation of Thermal Transport	Research Scientist	Massachusetts Institute of Technology, USA	2011.12.13-12.27
11SV5	Xincheng Xie	G. Bauer	Spin Hall and Spin Nernst Effects in Metals and Semiconductors	Professor	Oklahoma State University	2011.11.6-11.12

# Preparation of lead-free ferroelectric $\text{BaTi}_2\text{O}_5$ large-sized single crystals by floating zone melting

Chuanbin Wang, Rong Tu, Hirokazu Katsui, Kunio Yubuta and Takashi Goto\*

The transparent single crystalline  $\text{BaTi}_2\text{O}_5$  about 6 mm in diameter was successfully grown along *b*-direction by floating zone melting. The effect of foreign element substitution on the dielectric properties of  $\text{BaTi}_2\text{O}_5$  single crystals was investigated.  $\text{BaTi}_2\text{O}_5$  is a promising lead-free ferroelectric material used at higher temperatures due to the high permittivity and the high Curie temperature.

Although the phase diagram of BaO-TiO<sub>2</sub> system has been studied for a long time, the ferroelectricity of  $\text{BaTi}_2\text{O}_5$  ( $\text{BT}_2$ ) has not been known until recently. Our group and Akishige *et al.* independently synthesized single-crystalline  $\text{BT}_2$  and reported the significant ferroelectricity only in the *b*-direction. Since  $\text{BT}_2$  can be easily decomposed into  $\text{BaTiO}_3$  (BT) and  $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$  ( $\text{B}_6\text{T}_{17}$ ) above 1500 K, large-scaled single crystalline  $\text{BT}_2$  can be hardly prepared. In order to apply  $\text{BT}_2$  for practical applications, the process to prepare *b*-direction oriented  $\text{BT}_2$  single crystal in large scale should be developed.

Dried  $\text{BaCO}_3$  and  $\text{TiO}_2$  powders (purity: 99.99%) were weighed and mixed at the molar ratio of 1 to 2 exactly. A floating zone (FZ) melting apparatus with a xenon heating lamp was used to prepare single crystalline  $\text{BT}_2$ . The crystal phase was identified by X-ray diffraction (XRD). The dielectric properties were measured in air with an impedance analysis (Hewlett Packard 4194A) from 293 to 1073 K in a frequency (*f*) range between  $10^2$  and  $10^7$  Hz. A gold paste and wire was used as electrodes.

The as-grown single crystalline  $\text{BT}_2$  was transparent and its size was 6 mm in diameter and 30 mm in length. Figure 1 shows the appearance of single crystalline  $\text{BT}_2$  prepared by FZ, which was cut perpendicular to the growth direction, *i.e.*, *b*-direction.  $\text{Ba}_{0.99}\text{Sr}_{0.01}\text{Ti}_2\text{O}_5$  ( $\text{BST}_2$ ) single crystal 4 mm in diameter and 16 mm in length was also obtained by the FZ. The SrO distribution in the as-grown single crystals prepared by



Fig. 1 Appearance of large-sized transparent  $\text{BT}_2$  single crystal prepared by FZ.

FZ melting was almost uniform ( $\pm 0.02\%$ ) except the initial and final growth regions.

The peak permittivity ( $\epsilon_{\text{max}}$ ) of single crystalline  $\text{BST}_2$  at Curie temperature ( $T_c$ ) changed depending on SrO content (*x*). The permittivity of the single crystalline  $\text{BST}_2$  showed sharp peaks at the  $T_c$  and increased with increasing *x* until 0.01. Figure 2 demonstrates the effect of *x* on the  $T_c$  and the  $\epsilon_{\text{max}}$  of single crystalline  $\text{BST}_2$ . The  $T_c$  of single crystalline  $\text{BST}_2$  decreased from 748 to 742 K with increasing *x* from 0 to 0.03. The  $T_c$  of BST decreased linearly from 405 to 392 K with increasing *x* from 0 to 0.03, implying more sensitive to the  $\text{Sr}^{2+}$  substitution compared to that of  $\text{BST}_2$ . The solubility limit of  $\text{Sr}^{2+}$  in  $\text{BaTi}_2\text{O}_5$  was much lower than that in  $\text{BaTiO}_3$  because of the more complicated crystal structure of  $\text{BaTi}_2\text{O}_5$ . The smaller solubility of  $\text{Sr}^{2+}$  in  $\text{BaTi}_2\text{O}_5$  may result in the smaller change of  $T_c$  than that in  $\text{BaTiO}_3$ . The maximum permittivity of single crystalline  $\text{BST}_2$  had the highest value of 42190 at *x* = 0.01.

The remnant polarization ( $P_r$ ) and coercive electric field ( $E_c$ ) of single crystalline  $\text{BaTi}_2\text{O}_5$  were  $1.4 \times 10^{-2} \text{ Cm}^{-2}$  and  $0.7 \times 10^6 \text{ Vm}^{-1}$ , respectively. The  $P_r$  and  $E_c$  of the single crystalline  $\text{BST}_2$  at *x* = 0.03 were  $4.8 \times 10^{-2} \text{ Cm}^{-2}$  and  $1.7 \times 10^6 \text{ Vm}^{-1}$ , which were much larger than that of single crystalline  $\text{BT}_2$ , respectively.

## Key Words

Lead-free ferroelectric  $\text{BaTi}_2\text{O}_5$ , Single crystal, Floating zone melting

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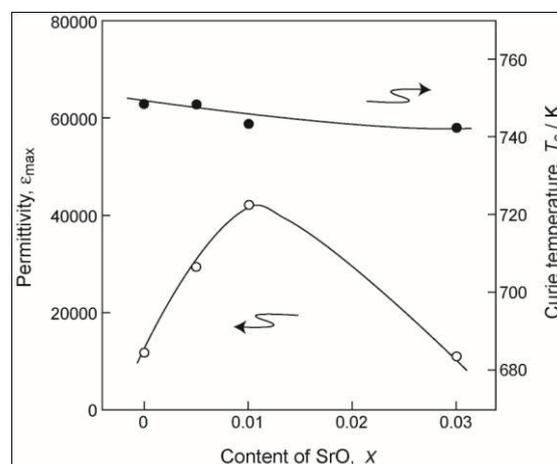


Fig. 1 Effect of SrO content in  $\text{BST}_2$  single crystal on the highest permittivity and Curie temperature.

## Neutron scattering study of collective triplet excitations in graphene based systems

Motivated by our analytical and numerical study of many-body excitations in graphene and graphite, we investigate the role of small spectral gap in the collective excitation spectra of graphene. We find that the single-particle gap parameter facilitates the formation of two collective states which are of singlet and triplet nature.

Graphene is a single layer of carbon atoms where  $2p_z$  electrons form symmetric spectrum of negative energy and positive energy states, described by the Dirac equation in 2+1 dimensions. Such a peculiar cone-like dispersion relation gives rise to plenty of intriguing phenomena in graphene which differs from their conventional metallic counterparts. The nature of particle-hole excitations in the semi-metallic state of graphene is also significantly different from the corresponding particle-hole continuum (PHC) in metals [1]. In analogy with the plasmonic excitations of metals, where (long range) Coulomb forces bind the particle-hole pairs to form collective states, within the equation of motion approach we find that a very similar treatment gives rise to bound state formation in the triplet particle-hole channel, albeit as a result of short range part of the Coulomb interactions [2].

The so obtained triplet branch of collective excitation below the incoherent continuum of particle-hole excitations in pristine graphene (Fig. 1) whose band structure is given by a clean cone-like dispersion turns out to pose challenges for the observation by neutron scattering experiments. The first challenge deals with the  $\sim 1\text{eV}$  energy scale associated with this branch of excitations, which requires very high energy incident neutron beam, such that the momentum transfer falls beyond the first Brillouine zone, where the rapidly decaying atomic form factor of spatially fat  $2p_z$  orbitals kills the neutron scattering signal [3]. On the other hand, if one focuses on the small energy parts of the spectrum, where lower energy incident neutrons are required, the expected coherent peak is so close to the incoherent PHC that in practice it does not seem easy to

isolate the peak corresponding to such a collective state.

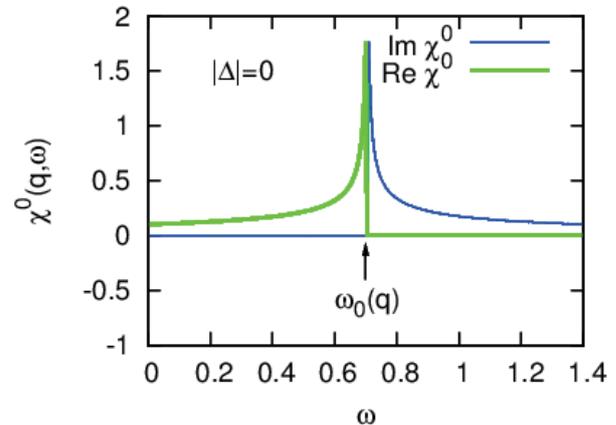


Fig. 1: The lower edge of the PHC is where the imaginary part of the non-interacting susceptibility (blue line) becomes non-zero. Energy scales is in units of the hopping  $t \sim 2.8$  eV of  $p_i$  electrons.

In this visit as suggested by my host, Professor K. Yamada, we examined the following question: what happens if for some reason, a single-particle gap is opened in the spectrum of Dirac fermions in graphene? As can be seen in Fig. 2, we find that as expected quite intuitively, the first role of gap opening is to push the lower edge of PHC to higher energies (where the blue line representing imaginary part becomes non-zero) and thereby to separate the incoherent part of the spectrum from the expected peak corresponding to collective excitations. However, we find that one more opportunity appears [4]; that is the density of particle-hole excitations is re-arranged in such a way that the real part (green line) displays a simple pole structure near the energy scale  $\omega_0(q)$  i.e. at the lower edge of the gapless spectrum. Therefore the intersection of the green plot will be possible with both  $1/U$  and  $-1/U$  which corresponds to collective excitations in triplet and singlet channels, respectively. Therefore the non-zero value of the gap parameter provides a room for the formation of an additional singlet (charge) collective mode. Our finding shows that these two modes disperse linearly as a function of their momentum with two different velocities [4].

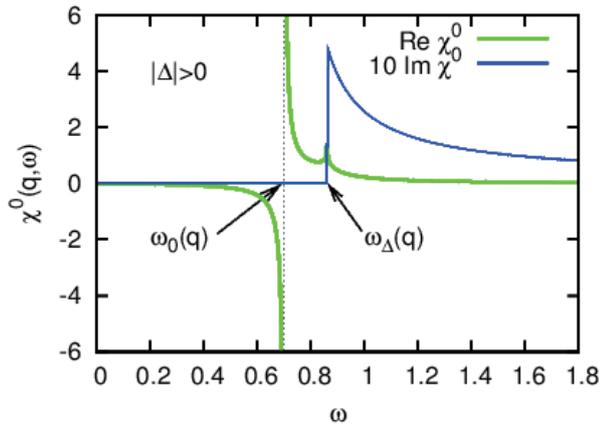


Fig. 2: The blue line is the onset of PH pair creation. As can be seen, gap opening pushes the edge of PHC to higher energies, but leaves behind a simple pole for the real part at the initial edge of the PHC.

The difference in the velocities is interpreted as the sign of spin-charge separation in the spirit of Luttinger liquids. The spin mode turns out to move faster than the charge mode. Beyond a critical value of short-range interactions the velocity of the charge mode becomes zero. We identify this as the onset of Mott transition where the charge excitations become localized, while low-energy spin excitations are still possible. This qualifies the gapped graphene as a candidate for a realization of spin liquids, where low-energy spin excitations are possible both in strong and weak coupling regimes. The prediction of the present study for the neutron scattering experiments in gapped Dirac systems (including graphene, highly oriented pyrolytic graphite etc) is that we expect two resonant peaks corresponding to singlet and triplet collective states [4]. The one with lower energy is the singlet state, and the one at slightly higher energy is the triplet state. Moreover the energy difference between them, provides a direct measure of the on-site Coulomb repulsion  $U$  of the material.

From an experimental point of view the gapped-graphane or Dirac-cone system is very attractive because of the existence of low energy magnetic and charge excitations which can be studied by using neutron and synchrotron beams. In the near future we will perform neutron and X-ray inelastic scattering experiments to detect low energy spin and charge excitations found by the present theoretical work.

## References

- [1] G. Baskaran and S. A. Jafari, Phys. Rev. Lett. **89**, 016402 (2002).
- [2] S. A. Jafari, G. Baskaran, J. Phys. Condens. Matter **24**, 09560 (2012).
- [3] S. A. Jafari, G. Baskaran, Eur. Phys. Jour. B **43**, 175 (2005).
- [4] S. A. Jafari, arxiv:1202.6499 (submitted for publication, 2012)

## Key Words

Gapped Dirac system, Spin-charge separation, Neutron scattering

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## Experimental Demonstration of a Persistent Current

By combining an epitaxial FePt nano-pillar with perpendicular magnetic anisotropy and a non-magnetic nano-ring, we will demonstrate an alternative method to generate a spin-polarised persistent current in a non-magnet. Even though such a spin-polarised persistent current has been proposed theoretically almost 20 years ago [1], there has been no experimental demonstration to date. This device would open up new horizon as a spin source for quantum computation.

Quantum phases of charged particles have been investigated in mesoscopic structures, and have revealed interference and oscillatory behavior induced by an external field application [2]. For instance, electrons travelling along semiconductor or normal metal rings threaded by a magnetic flux acquire a quantum dynamical phase, producing interference phenomenon such as the Aharonov-Bohm (AB) and Altshuler-Aronov-Spivak (AAS) effects. In addition, when the spin of electron rotates during its orbital motion along the ring-shaped path, the electron acquires an additional phase contribution known as the geometrical or Berry phase.

Recently, a geometrical phase has been predicted by studying electron transport under an inhomogeneous magnetic field. The geometrical phase can drive a persistent current. A pioneering experiment has been performed using spin-orbit scattering in a two-dimensional electron gas (2DEG) semiconductor, which also strongly couples spin and orbital motion and introduces a spin rotation. For metallic rings, it has been pointed out that electrons can sense the geometrical phase even when an effective exchange field is induced by ferromagnets. However, no results have been reported on the correlation between the geometrical phase and the presence of the ferromagnets. Interestingly, as opposed to a general belief that ferromagnets destroy quantum phase effects due to their complex dephasing mechanisms, an oscillatory behavior of resistance in a permalloy nanoring has been observed and an effect of ferromagnetic ordering in a GaMnAs semiconductor has been detected experimentally [3]. Such an AB oscillation in a ferromagnetic ring has been studied theoretically, suggesting that a dynamic phase can exist under the special condition when a ferromagnetic ring possesses perpendicular anisotropy. I have previously explored the effect of ferromagnets upon the electron quantum phase using a metallic nanoring, consisting of a trilayered FeNi/Cu/FeNi structure known as a current-in-plane (CIP) giant magnetoresistive (GMR) spin valve [4].

Previously we have fabricated FePt nanopillar encircled by a Au nanoring. At 350 mK, significant hysteresis was observed in the magnetoresistance when the magnetisation of the pillar was measured as shown in Fig. 2. The stray field from the pillar will act at a slight angle to the nanoring because the two objects do not lie in exactly the same plane. This will induce a persistent current in the ring. The simple 4-terminal configuration shown in Fig. 1 then allows the persistent current to be detected. The persistent current was observed via the hysteresis in the magnetoresistance when the magnetisation of the pillar was

measured.

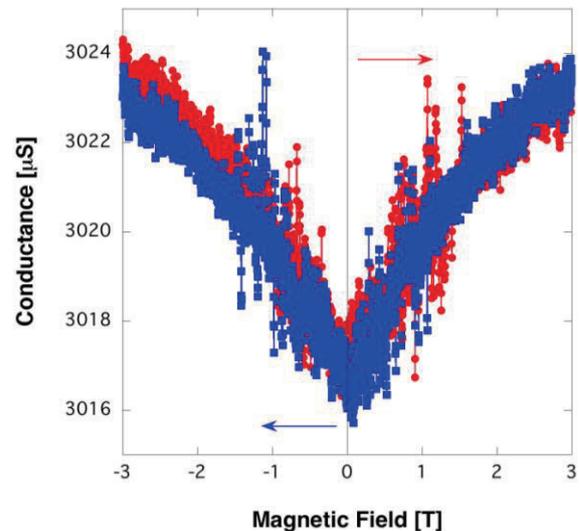


Fig. 1 Magnetoresistance of the quantum device at 350 mK.

We have further improved a new nanofabrication method has been successfully developed to produce a 260-440-nm-inner-diameter Ag nanoring and a 50-120-nm-diameter FePt nanopillar inside by using electron-beam lithography and Ar-ion milling. As shown in Fig. 1, the center nanopillar is designed to provide a non-uniform magnetic field in the nanoring at its remanent state after perpendicular saturation. Such a non-uniform field is theoretically expected to induce a persistent spin current in the nanoring [1]. The induced current is intended to be measured by four contacts fabricated near the nanoring.

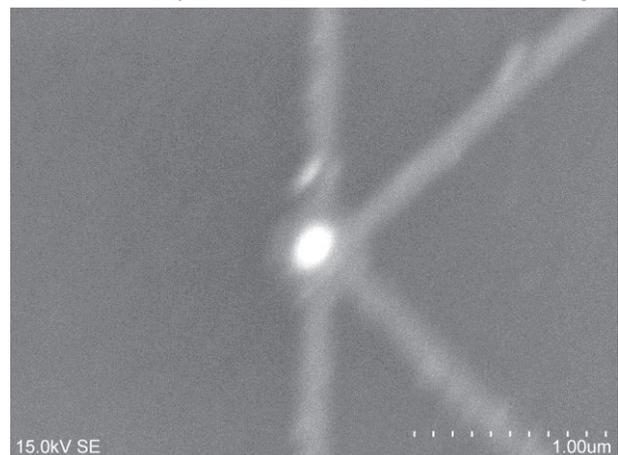


Fig. 2 SEM image of a quantum device.

We now plan to observe new quantum phenomena by measuring nanoscale spintronic devices at below 500 mK. We will first detect the observation of the AB signals to confirm the quality of the devices. Accordingly, we will focus on a persistent current induced in a non-magnetic nanoring under a non-uniform magnetic field application as predicted in Ref. [1].

### References

[1] D. Loss and P. M. Goldbart, *Phys. Rev. B* **45**, 13544 (1992).

[2] Y. Imry, *Introduction to Mesoscopic Physics* (Oxford University Press, Oxford, 1977).

[3] L. Vila *et al.*, *Phys. Rev. Lett.* **98**, 027204 (2007).

[4] K. Sekiguchi *et al.*, *Phys. Rev. B* **77**, 140401(R) (2008).

**Key Words**

Persistent current, Spin-polarised electrons, Word3

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## Title: Thermal transport from first-principles

*Abstract: Unlike electronic properties, the calculation of the lattice thermal conductivity from first-principles is not that straightforward. We have developed a methodology to perform these calculations [1,2], and have applied it to several materials including Si, GaAs, PbTe, PbSe, and ZrCoSb. We intend to pursue this path and also calculate the thermal transport properties of new thermoelectric materials such as GeSe.*

Research on thermoelectric materials was revived in the 90's [3] after realizing that in low-dimensional systems, the sharp variations in the density of states can lead to a large Seebeck coefficient. For energy conversion using thermoelectric materials, or in thermal barrier coatings used in aerospace industry, one needs to have a low thermal conductivity material. For optoelectronics applications, on the other hand, high thermal conductivity materials are required so that the generated heat from currents can be quickly evacuated. Management of heat is therefore of paramount importance for technological applications. In semiconductors used in thermoelectric devices, heat is mostly carried by phonons. One can interpret the standard Boltzmann formula within the relaxation time approximation, as the thermal conductivity coming from different phonon modes, each carrying an amount of heat proportional to the mean free path (MFP), group velocity and heat capacity of that mode. Accordingly, acoustic modes carry more heat than optical one because of their larger group velocity and larger MFP. The latter is inversely proportional to the phonon scattering rate, itself determined from the Fermi's golden rule (FGR). At high temperatures, phonons scattering is dominated by 3-phonon processes. The probability of such processes depend on the strength of the phonon-phonon coupling dictated by the cubic force constants. We have used first-principles density functional theory (FP-DFT) to compute accurately the harmonic and cubic force constants (FCs). The former is used to obtain the phonon frequencies and group velocities, and the latter provides the phonon lifetimes through FGR. The methodology to extract the FCs from FP-DFT calculations in a supercell is detailed in [1] while the calculation of the phonon lifetimes and thermal conductivity is described in [2]. We applied this methodology to Si [2], PbTe, GaAs and half-Heusler compounds such as ZrCoSb. The results were discussed in [4]. In figure 1 we show the calculated thermal conductivities of these materials as compared with experiments. We can note that the agreement is within 10% or less in the studied cases. Figure 2 shows the contribution of the phonons of different MFP to the total thermal conductivity.

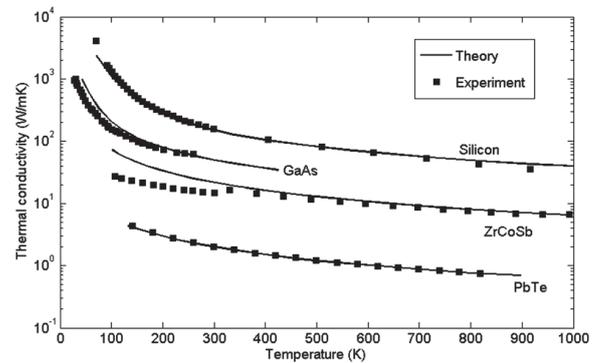


Fig. 1 Thermal conductivities of several materials versus T.

It can be seen that in Si for example, phonons of MFP more than 1000 nm contribute almost to half of the thermal conductivity at room temperature. This information is very useful in designing nanostructured materials of desired thermal properties. In Si, if the nanostructure size is 100 nm, the thermal conductivity will almost be reduced by a factor of 4, while this size does not affect much thermal transport in PbTe or ZrCoSb.

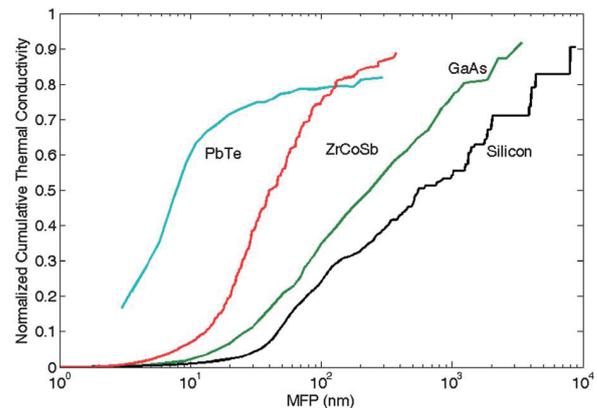


Fig 2. Accumulated thermal conductivity versus the mean free path for the same materials as in Fig 1. at T=300K

### References

- [1] K. Esfarjani, H.T. Stokes, *Phys. Rev. B* **77**, 144112 (2008).
- [2] K. Esfarjani, G. Chen and H.T. Stokes, *Phys. Rev. B* **84**, 085204 (2011)
- [3] L. D. Hicks and M. S. Dresselhaus, *Phys. Rev. B* **47**, 12727 (1993); **47**, 16631 (1993)
- [4] M. Zebarjadi, K. Esfarjani, M.S. Dresselhaus et al., *ENERGY & ENVIRONMENTAL SCIENCE* **5**, 5147 (2012)

### Key Words

Thermal transport, thermoelectricity, phonon mean free paths

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## Spin superconductor in ferromagnetic graphene

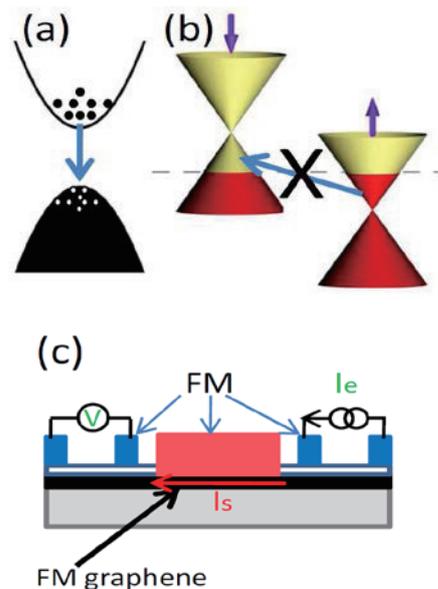
### Abstract

We show a spin superconductor (SSC) in ferromagnetic graphene as the counterpart to the charge superconductor, in which a spin-polarized electron-hole pair plays the role of the spin  $2(\hbar/2)$  'Cooper pair' with a neutral charge. We present a BCS-type theory for the SSC.

### Body

Superconductivity is well understood by BCS theory: Electrons in a solid state system may have a net weak attraction so that they form Cooper pairs, which can then condense into the BCS ground state. The simplest s-wave Cooper pairs are of electric charge  $2e$  and spin singlet. A dual of superconductor is the so-called exciton condensate in which a Cooper pair-like object is a particle-hole pair which is charge-neutral while its spin may either be singlet or triplet. We name a spin-triplet exciton condensate as the spin superconductor (SSC). Ferromagnetic (FM) graphene contains an imbalance of up and down spins that can be injected, e.g., by ferromagnet contacts (Fig. 1 (b)). When the Fermi level lies in between the spin-resolved Dirac points, the spin-up carriers are electron-like while the spin-down ones are hole-like. These positive and negative carriers attract and form e-h pairs that are stable against the e-h recombination due to the Coulomb interaction, unlike in conventional exciton systems in semiconductors (Fig. 4(a)) where the electron states are above the hole states. If a carrier jumps from the electron-like state to the hole-like one, the total energy of the system rises. This prevents the e-h recombination and means the e-h pairs in FM graphene is stable and can exist indefinitely in principle. Therefore, this e-h pair gas can condense. The ground state of FM graphene is a neutral superfluid with spin  $\hbar$  per pair, namely, a SSC state.

For detection of the SSC, one can measure the zero spin resistance or super spin current. Here we propose a four terminal device as shown in Fig.1(c) which can be used to measure the non-local resistance and then confirm the SSC state.



**Fig. 1:** The schematic diagrams for (a) the band structure for the conventional exciton system; (b) for FM graphene; and (c) for the proposed four-terminal device to measure the SSC state.

### Reference

1. Q.F. Sun, Z.T. Jiang, Y. Yu, and X. C. Xie, Phys. Rev. B **84**, 214501 (2011)

### Keywords

Graphene, superconductivity

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Activity Report

# Young Researcher Fellowships



## FY 2011 Young Researcher Fellowships

No.	Name	Host	Proposed Research	Title	Affiliation	Term
11FS1	Jonathan Nguyen	H. Kato	Enhanced Mechanical Behavior of Zr-Cu-Al-Ag with Addition of MWCNT via Wet Processing	Ph. D. Student	University of California, Davis, USA	2011.8.18-24
11FS2	Dazhi Hou	E. Saitoh	Electronic Manipulation of Spin Current between Metal and Insulator	Ph. D. Student	Fudan University, China	2011.11.5-2012.3.31

## Synthesis and Dispersion of Carbon Nanotubes on Cu-Based Bulk Metallic Glass Powder

### Abstract:

Bulk metallic glasses (BMGs) generally exhibit brittle behavior. The current research examines the hypothesis that a dispersion of nanotubes may alleviate the ductility issue. Specifically, the current study provides insight into the dispersion behavior of carbon nanotubes onto  $\text{Cu}_{50}\text{Zr}_{50}$  (CZ) and  $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$  (CZA) in a surfactant solution. It has been shown that dispersion quality and behavior vary as a function of dwell time in solution.

### Body:

Bulk metallic glasses exhibit attractive combinations of physical and mechanical properties; however, they tend to fail in a brittle manner [1, 2]. It has been shown that reinforcement with secondary phase dispersions can enhance ductility along with strength, toughness, and hardness [3, 4]. The enhanced ductility in BMG-CNT composites is attributed to a mixed structure that obstructs shear band flow deformation which concomitantly increases strength. The research performed through the ICC-IMR Young Scientist Fellowship allowed for synthesis of BMG powder as well as spectroscopic characterization studies.

Synthesis of BMG-CNT composites involves the following steps: 1) Producing ingots using vacuum arc melting of high purity elemental metal powder of the desired nominal composition in a Ti-gettered Ar purified environment, 2) Pre-alloyed ingots are gas atomized for powder synthesis, 3) BMG powders are mixed with surfactant solution for CNT dispersion, 4) Spark Plasma Sintering (SPS) is used to consolidate the composite powders into bulk form.

Production of CZ and CZA powders were achieved using high pressure gas atomization with He and Ar as cooling gases, respectively. Figure 1 shows XRD of both CZ and CZ-CNT powders. The binary alloy has a smaller glass transition region, therefore had a lower yield and was overall more difficult to produce in fully amorphous form as indicated by the  $\text{Cu}_2\text{Zr}$  peaks.

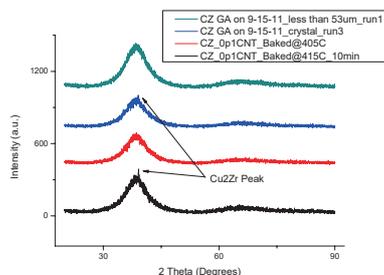


Figure 1 – XRD scan of  $\text{Cu}_{50}\text{Zr}_{50}$  powder, peaks indicate crystalline phase of  $\text{Cu}_2\text{Zr}$  present in some cases

Following the powder atomization experiments, spark plasma sintering (SPS) was used to consolidate the powder into bulk form. Although there was insufficient time to achieve full density of either CZ or CZA powders, continued work on process parameter optimization at University of California, Davis has made great progress towards achieving this goal. Figure 2 shows SPS samples with densities of 94% on the left and 89% on the right. The as-SPSed mirror like finish and sharp well define edges around the circumference of the disk indicates the processing conditions are nearly optimal to achieving densities of greater than 98%.

Future work on these powders include achieving nearly full density of all powder types, mechanical behavior testing to determine the overall contribution of CNTs in a BMG structure, and SEM/TEM analysis of morphology of BMG-CNT interface.



Figure 2 – (Left) SPSed CZA sample with 94% density (Right) SPSed CZA sample with 89% density

### References

1. Sun, Y.F., et al., *Journal of Materials Research*, 2005. **20**(9): p. 2386-2390.
2. Xie, G., et al., *Scripta Materialia*, 2006. **55**(8): p. 687-690.
3. Bian, Z., et al., *Advanced Functional Materials*, 2004. **14**(1): p. 55-63.
4. Hofmann, D.C., et al., *Nature*, 2008. **451**(7182): p. 1085-1089.

### Key Words

Carbon Nanotube, Bulk Metallic Glass, Dispersion

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# ICC-IMR FY2011 Activity Report

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