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KINKEN Research Highlights 2015

Institute for Materials Research, Tohoku University



Research

KINKEN

Research Highlights

2015



Institute for Materials Research, Tohoku University

KINKEN Research Highlights 2015

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Preface

Dear Colleagues,

We are pleased to present *KINKEN* Research Highlights 2015, which is the annual report that includes a collection of research outputs of the past year from the Institute for Materials Research (IMR), Tohoku University. *KINKEN* is the abbreviation for “Kinzoku Zairyo Kenkyujo,” the Japanese name for IMR, which is well known in the materials science community.

Professor Kotaro Honda established the IMR at the Tohoku Imperial University in 1916 as the 2nd Division of the Provisional Institute of Physical and Chemical Research. At that time the primary research focus was steel. Thereafter, the research domains gradually broadened to include various types of alloys and metals. The name was changed into the Research Institute for Iron, Steel and Other Metals (RIISOM) in 1922. Subsequently, the institute developed into a global center for fundamental and applied research covering all types of materials, including nonmetals. In 1987 the institute was reorganized into a national collaborative research institute affiliated with Tohoku University, and consequently renamed to the present Institute for Materials Research (IMR).

IMR has greatly contributed to the advancement of materials science and engineering. The invention of KS steel in 1916, the strongest permanent magnet at that time, was the first great achievement. In subsequent years, many different types of practically useable materials have successfully been developed, including new KS steel, Sendust alloy, SiC fibers, various intermetallic compounds, and more recently, amorphous alloys. In addition, considerable effort was dedicated to basic research for materials development, which paved the way for pioneering research in magnetism, superconductivity,



Director



optical properties, and microstructure analyses of materials. Recently, IMR has created a wide array of new materials, including high-performance, high-quality, and multifunctional materials such as bulk metallic glasses, nanostructured materials, nanocomposites, ceramics, crystals, oxides, nitrides, hydrides, complexes, organic materials, etc., which are useful for electronic, optical, magnetic, spintronic, biological, energetic, and infrastructural applications.

In the 21st Century, we face worldwide environmental problems such as global warming and the depletion of resources and energy. There is an increasing need to preserve the environment and work towards achieving sustainable societies. IMR upholds these themes with the objective of “contributing to the well being of the human race and the development of civilization through the creation of new materials that are truly useful to society”.

We hope that the KINKEN Research Highlights will enable you to better understand our recent research activities and will aid the promotion of worldwide collaboration with IMR. We ask for your continued support and welcome any suggestions.

Infrastructural Materials

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Controlling Phase Transformation of Steels using Microalloying Elements

Advanced high-strength steels with high toughness are demanded for reliable construction and for lowering the weight of automobiles. Microalloying technology, that is, addition of very small amounts of specific elements such as B and Mo, has been developed to control properties of steels. In our group, the effects of microalloying on phase transformation kinetics have been investigated systematically. Here, we show strong effects of addition of a small amount of B and Mo, and their local enrichment at interphase boundaries.

More than 100 million tons of steel is produced every year in Japan for use in industries such as automobile, construction, and vessels. In order to achieve the various properties required for these applications, novel alloy designs combined with sophisticated thermomechanical treatments have been developed. It is known that the addition of a very small amount of specific alloying elements, such as Nb, B, and Mo can change the kinetics of phase transformation significantly, and thus, influence the mechanical properties. Such a “microalloying” technique has been attracting much attention because of a strong demand in developing advanced high-strength steels with reduced amount of elemental consumption.

Recently, our group has studied the effects of microalloying Mo, Nb, and B to low-carbon welding steels [1-3], since the microalloying of these elements effectively yields a bainite structure in low-carbon, low-alloy steels under slow cooling, which is important for strengthening steels. Figure 1 shows a significant influence of a very small amount of Mo (0.5%) and Boron (10 ppm) on bainite transformation kinetics. It was found that bainite transformation is suppressed strongly by the addition of Mo while the effect of B is small. On the other hand, a synergetic effect appears by the combined addition of B and Mo. In order to clarify the mechanism of the retarding effect of Mo on bainite transformation, element segregation at the bainite/matrix interface boundaries are investigated using aberration-corrected scanning TEM/EDS (Fig. 2). In the early stage of transformation (Fig. 2(a)), there is no segregation of either Mn or Mo at the boundaries. At the onset of stasis of transformation (Fig. 2(b)), only a small segregation of Mn is seen, whereas Mo does not exhibit a detectable enrichment. Remarkable segregation of Mo and Mn takes place at longer holding time (Fig. 2(c)).

Since there is clearly a time lag between the beginning of transformation stasis and the beginning

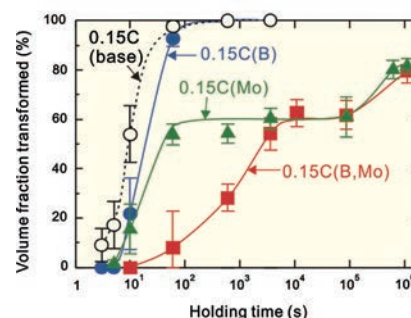


Fig. 1 Effect of a small amount of Mo (0.5%) and B (10 ppm) on transformation kinetics [2].

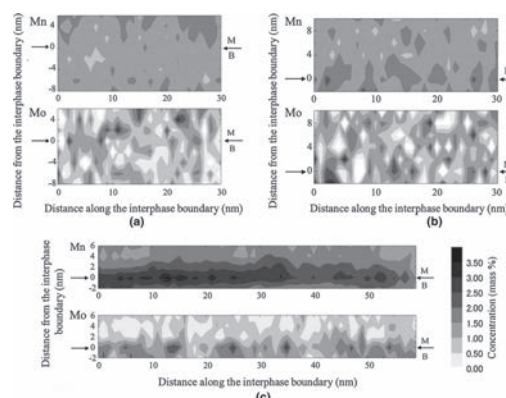


Fig. 2 Element segregation at the interphase boundary in the specimen with Mo transformed for (a) 10 s, (b) 60 s, and (c) 1.8 ks [2].

of Mo segregation, this suggests that the effect of Mo segregation at the interface is weak, despite the marked effect of the Mo in the appearance of transformation stasis.

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Structural Modeling of Fe₈₀B₂₀ Amorphous Alloy by Using AXS Technique

The three-dimensional structural model of an Fe₈₀B₂₀ amorphous alloy was simulated using a reverse Monte Carlo (RMC) simulation using a combination of anomalous X-ray scattering (AXS) and neutron diffraction (ND). The fundamental structural features agree well with those obtained using the common dense random packing (DRP) model. However, the atomic arrangement around B is characterized by an anti-prism-like cluster [1].

Fe-based metal-metalloid amorphous alloys are used as soft magnetic materials. Their glass-forming abilities are associated with the atomic arrangement of constituents [2]. We prepared an ingot with a nominal quantity of Fe₈₀B₂₀ by the conventional arc melting of a mixture of pure iron (99.99%) and boron (99.4 % ¹¹B). Ribbon samples of thickness ~20 μm and width 1 mm were prepared using a melt-spinning technique. Ordinary X-ray diffraction and AXS for the Fe K-absorption edge were carried out at the BL-7C beam-line of the Photon Factory at IMSS. The $\Delta Q_{\text{Fe}}(Q)$ and $Q_i(Q)_{\text{X-ray}}$ interference functions were obtained from the observed scattering intensities. The $Q_i(Q)_{\text{neutron}}$ function was also obtained by using the time-of-flight technique at NOVA of MLF, J-PARC. Three interference functions were used to model the atomic arrangement by applying the AXS-ND-RMC method. An initial model, consisting of 10,000 atoms (Fe: 8000 and B: 2000) placed within a cubic hypercell ($L = 4.737$ nm, 7.32 Mg/m³), was produced using the DRP model of hard spheres.

Figure 1 shows the experimental and calculated interference functions $\Delta Q_{\text{Fe}}(Q)$, $Q_i(Q)_{\text{X-ray}}$, and $Q_i(Q)_{\text{neutron}}$. There is no pre-peak signal at the lower Q -region, indicating the tendency for compound formation. The fundamental atomic arrangement can then be well demonstrated using a random packing structure. To determine the local structural units, further advanced AXS-ND-RMC modeling was carried out under experimental constraints for the obtained interference functions. Although the previous study reported the first B-B distance of about 0.355 nm [3], the present AXS-ND-RMC modeling indicates a shorter nearest-neighbor B-B correlation at 0.21 nm. The Voronoi polyhedral analysis around Fe clearly shows that the deformed-fcc and icosahedron-like local structural units are common, and this feature is readily reproduced by the common DRP model. On the other hand, the atomic arrangement around B prefers an anti-prism-

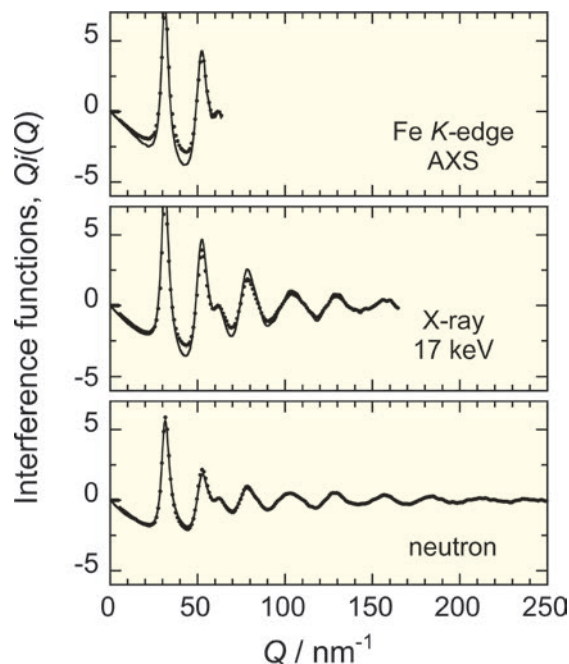


Fig. 1 Three interference functions for Fe₈₀B₂₀ amorphous alloy. Solid lines: experimental data. Dotted lines: AXS-ND-RMC results.

like coordination. These characteristic local structures in Fe₈₀B₂₀ represent the chemical short-range order around B.

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Wear Behavior of Biomedical Titanium Alloys in Simulated Body Fluid and Air

Wear behavior of combinations comprised of an ($\alpha+\beta$)-type titanium alloy, Ti-6Al-4V ELI (Ti64) and a β -type titanium alloy, Ti-29Nb-13Ta-4.6Zr (TNTZ) in simulated body fluid and air were investigated for biomedical applications. Although the volume loss of metallic materials often increases in air compared to simulated body fluid, the volume loss in simulated body fluid is larger than that in air for TNTZ disc/TNTZ ball combination. In this case, delamination wear is predominant for this combination. On the other hand, the predominantly abrasive wear occurs in a Ti64 disc/Ti64 ball combination so that its volume loss in simulated body fluid is less than that in air.

Titanium alloys are currently used for biomedical applications because of their excellent mechanical properties and biocompatibility. Such applications sometimes include components with metal-to-metal contact, although wear resistance of titanium alloys is generally poor. It is well known that wear occurring in human body induces implant loosening, and the presence of wear debris causes inflammatory reactions, resulting in pain in the patient. Thus, an improvement in wear resistance is required for biomedical titanium alloys so that wear characteristics of titanium alloys can be understood to improve their wear properties.

Two types of titanium alloys were examined in this study. The first is a conventional ($\alpha+\beta$)-type Ti-6Al-4V ELI alloy (Ti64), which accounts for approximately 45–60% of the total titanium alloys produced globally, and the second is a β -type Ti-29Nb-13Ta-4.6Zr alloy (TNTZ) developed for biomedical applications, which is comprised of only non-toxic and allergy-free alloying elements, and lower Young's modulus compared to that of Ti64.

Figure 1 shows the volume loss of discs and balls made of Ti64 and TNTZ subjected to the frictional wear tests in simulated body fluid, Ringer's solution at 310 K [1], and air at room temperature [2]. When the TNTZ disc slides against the TNTZ ball, the volume loss of both the disc and ball is the maximum in both Ringer's solution and air. In addition, although the volume loss often decreases in Ringer's solution compared to air because Ringer's solution can act as a liquid lubricant during sliding, the volume loss in Ringer's solution increases compared to that in air for the TNTZ disc/TNTZ ball combination.

In order to clarify the difference in the wear behaviors between the TNTZ disc/TNTZ ball and the Ti64 disc/Ti64 ball combinations, morphological analysis of the wear debris collected from the discs

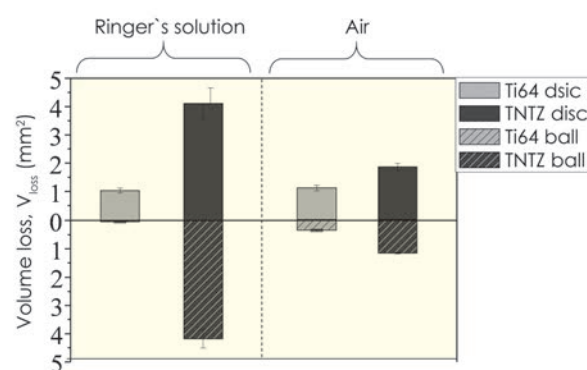


Fig. 1 Volume losses of Ti64 and TNTZ discs and balls obtained from frictional wear tests in Ringer's solution and air.

and balls at the end of frictional wear tests in Ringer's solution and air was performed. Cutting chip-like wear debris were observed in the Ti64 disc/Ti64 ball combination, indicating that a microcutting action occurs during sliding. This result suggests that abrasive wear occurs in both Ringer's solution and air for this combination. In contrast, large amounts of flake-like wear debris were observed in the TNTZ disc/TNTZ ball combination, indicating that delamination wear occurs in both Ringer's solution and air. Therefore, it is considered that the volume loss during the frictional wear tests is enhanced in Ringer's solution compared to air when delamination wear is predominant for each combination.

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Laser Oscillations from Transparent Polycrystalline Ceramics Produced by Spark Plasma Sintering

Laser oscillations were demonstrated for the first time using Nd^{3+} -doped Lu_2O_3 transparent polycrystalline ceramics produced by spark plasma sintering. The laser performance confirms that spark plasma sintering is a promising technique for producing laser-quality transparent ceramics.

Transparent polycrystalline ceramics are promising optical media for solid-state lasers and scintillators. Spark plasma sintering is an advantageous technique for producing transparent polycrystalline ceramics because of a faster densification process compared to conventional sintering methods.

Although extensive research have been undertaken on the preparation of transparent polycrystalline ceramics using spark plasma sintering, no one has successfully demonstrated laser oscillation thus far. For the spark plasma sintering process, a short holding time and a low sintering temperature prevent grain coarsening and favor the fabrication of fine-grained ceramics with high transparency. However, a deep understanding is required for optimizing powder processing and sintering parameters to produce a laser-quality transparent ceramic by inhibiting the defect formation and eliminating pores.

We proposed the two-step pressure sintering combined with a low heating rate to produce transparent Lu-based oxides, such as Lu_2O_3 [1], $\text{Lu}_2\text{Ti}_2\text{O}_7$ [2], Lu_3NbO_7 , and $\text{Lu}_3\text{Al}_5\text{O}_{12}$. The preload pressure affected the intermediate relative density, and the transmittance in the visible range was more sensitive to preload pressure than that in the infrared range. The combination of the low heating rate and the two-step pressure profile resulted in a high transparency (Fig. 1(a)).



Fig. 1 (a) Lu_2O_3 and (b) Nd^{3+} -doped Lu_2O_3 transparent polycrystalline ceramics produced by spark plasma sintering. The diameter of the ceramics is 10 mm.

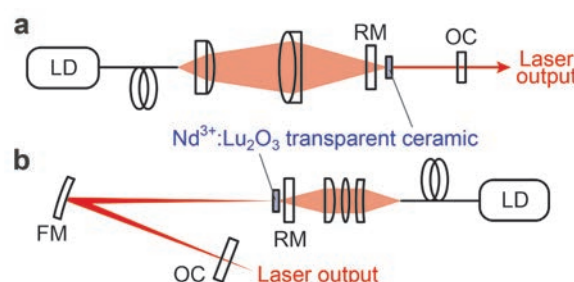


Fig. 2 (a) Straight-type and (b) V-type laser cavities for end-pumping configurations with fiber coupled diode laser (LD) sources. OC: output coupler, RM: rear mirror, and FM: folding mirror.

We report another discovery that LiF can promote reaction sintering and eliminate carbon contamination through vaporization of LiF at elevated temperatures [3]. Nd^{3+} -doped Lu_2O_3 ceramic with 0.2 wt% LiF showed a transmittance of 99.5% of the theoretical at $\lambda = 1080 \text{ nm}$ (Fig. 1(b)), which corresponds to the laser lines with $^4\text{F}_{3/2}$ to $^4\text{I}_{11/2}$ transition.

Laser oscillations were demonstrated by two-types of laser cavities using end-pumping configurations (Fig. 2) [4, 5]. For example, the obtained maximum output power was 0.2 W, and the slope efficiency was 14%, which is comparable to that of Nd^{3+} -doped Lu_2O_3 ceramics and single crystals [4]. These laser performances confirm that spark plasma sintering is a promising technique for producing laser-quality transparent ceramics.

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FCC (γ) $\rightarrow$ HCP (ϵ) Martensitic Transformations Dominate Strain and Damage of Co–Cr–Mo Alloy with Negative Stacking Fault Energy

Co–Cr–Mo alloys have been used for various biomedical implants such as artificial hip and knee joints. Negative stacking fault energy (SFE) of the alloy gives rise to unique mechanical behaviors, which differentiate the alloy from other conventional FCC alloys. Here, we introduce the FCC (γ) $\rightarrow$ HCP (ϵ) martensitic transformations, originating from the negative SFE, in strengthening and fatigue behaviors.

Local strains developed by athermal $\gamma \rightarrow \epsilon$ martensitic transformation were investigated for Co–29Cr–6Mo (wt%) alloys with or without added nitrogen [1]. Electron backscatter diffraction (EBSD) based strain analysis revealed that the N-free alloy consisting of the γ matrix and athermal ϵ -martensite plates showed large elastic and plastic strains in the γ matrix. Transmission electron microscopy (TEM) (Fig.1) showed the ϵ -martensite plates were aggregates of thin ϵ -layers formed by three different Shockley partial dislocations that canceled each other's shear strains. We have revealed that the elastic strains in the γ matrix originate from interactions among the ϵ -martensite phase, extended dislocations, and/or thin ϵ -layers. The dislocations highly dissociated into stacking faults, making stress relaxation at intersections difficult and further introducing local strain.

The mechanism of extrusion and intrusion formation, which causes fatigue fracture, was investigated with special focus on the role of the strain-induced $\gamma \rightarrow \epsilon$ martensitic transformation (SIMT) (Fig. 2(a)) [2]. We found that the SIMT leads to extrusions and intrusions whose morphologies were quite different from those seen in other γ alloys (Fig. 2(b) and (c)), and it was attributed to the localization of plastic strain within thin layers of SIMT ϵ -phase. Also, it was found that the localization of plastic strain could be avoided by decreasing the grain size, and the techniques of grain refinement is important not only for increasing the tensile strength but also improving fatigue strength. These findings are important for producing reliable devices by electron beam additive manufacturing (*i.e.* 3D printing) in which coarse grains are formed [3].

Based on these fundamental studies, we are developing novel technologies for improving the properties, such as the heat treatment decreasing grain size after fabrication with keeping the shape [4]. Also, we are extending the application area of Co–Cr–Mo alloy to the fields beyond the biomedical area, including metal die-casting, injection-molding, and fuel-cell application [5]. Moreover, novel Co–Cr based

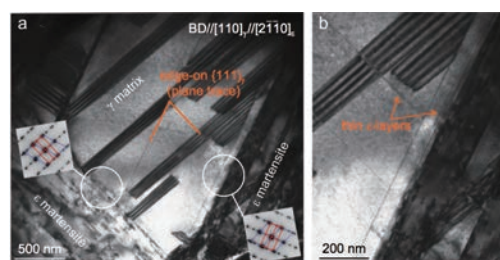


Fig. 1 (a) TEM image showing interfaces between γ matrix and ϵ martensite in N-free Co–29Cr–6Mo alloy quenched from 1473 K. (b) Magnified image of γ/ϵ interface growing through nucleation and densification of thin ϵ -layers.

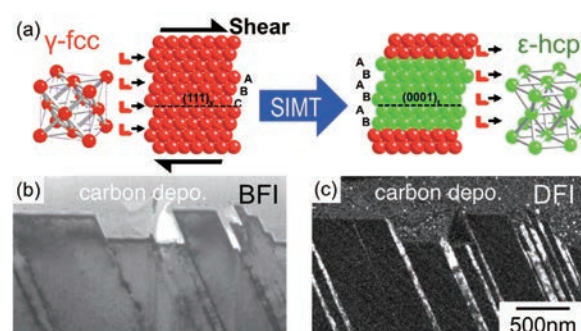


Fig. 2 (a) Schematic of SIMT and cross-sectional TEM, (b) bright field image (BFI) and (c) dark field of surface reliefs on fatigued Co–Cr–Mo alloy [2].

alloys consisting other elements, such as Co–Cr–W alloy, are being developed [6].

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Synthesis of Ultrafine-grained Copper Alloys with Nanoscale TiC Dispersion by High Energy Ball-Milling and Hot Pressing

Copper is being widely used in industries because of its high electrical and thermal conductivity, and excellent resistance to corrosion. Considerable efforts have been directed to the development and design of novel copper-based alloys exhibiting high electrical conductivity and mechanical strength for practical applications. The nanoscale TiC-strengthened copper alloys were manufactured by an internally developed two-step ball-milling process, and the properties at room and elevated temperature were investigated.

Recently, many studies have been conducted to design new copper-based alloys with high electrical conductivity and high strength using precipitation- and dispersion-strengthening methods. However, it has been proven that dispersion strengthening is more effective in providing outstanding properties at elevated temperatures, as precipitates could coarsen or dissolve into the copper matrix at elevated temperatures.

In this study, TiC was selected as the reinforcing particle because of its high melting point, high thermal, and chemical stability. The mechanism for high conductivity and high strength was analyzed (Fig. 1) [1]. The Ti-C reaction leads to a highly purified matrix, which guarantees high conductivity. It was found that the carbon particle size plays a significant role in the formation of TiC during the process. The ultrafine-grained (UFG) microstructure with an average grain size of around 300 nm

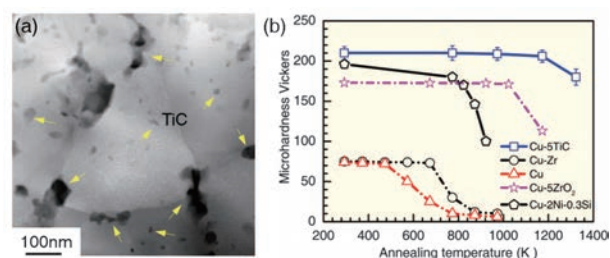


Fig. 2 (a) Representative microstructure showing UFG microstructure and nanoscale TiC particles, and (b) microhardness of the prepared samples compared to other Cu materials after 1 h annealing at different temperatures.

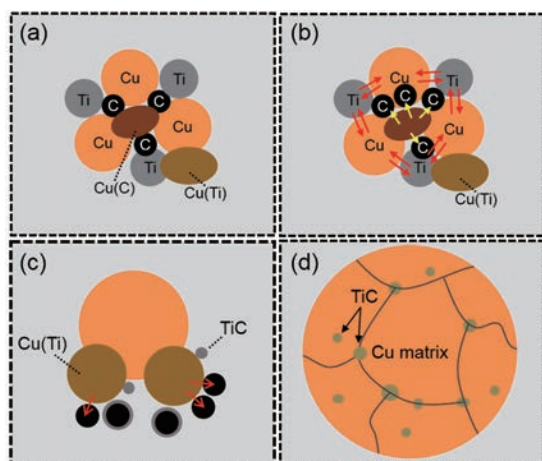


Fig. 1 Reaction mechanism for high conductivity and strength of Cu-Ti-C system: (a) Fine-grained mixture of Cu-Ti-C after ball-milling; (b) Interdiffusion of Cu and Ti, dissociation of the supersaturated Cu(C) during spark plasma sintering (SPS); (c) Chemical reaction of Ti-C during SPS and heat treatment; (d) Final microstructure.

developed in this process [2], and the nanoscale TiC particles in the grain interior result in high strength through the Hall-Petch and Orowan strengthening mechanisms, as shown in Fig. 2(a). The manufactured Cu-TiC alloys showed a combination of conductivity-tensile strength of around 71%IACS-712 MPa. Furthermore, the TiC particles located at the grain boundaries could contribute to the thermal stability by the Zener pinning effect. Stagnation of the matrix grain growth was observed through annealing experiments at different temperatures, and the room temperature microhardness compared to other Cu-based materials after 1 h annealing was analyzed (Fig. 2(b)). Compared to other Cu materials, the prepared alloys showed excellent thermal stability at the annealing temperature of 1223 K, while there is only a slight drop in HV with annealing temperature of 1323 K for 1 h.

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Microstructure and crystallographic features of nodular bainite in the Cu-Sn alloy system

We have investigated the microstructure and orientation relationship (OR) of the α and δ phases in an as-cast ingot and nodular bainite of Cu-14.9 at% Sn alloy using transmission electron microscopy (TEM). It was found that the α and δ phases in nodular bainite exhibit both $(111)_\alpha // (110)_\delta$, $[\bar{1}\bar{1}1]_\alpha // [\bar{1}\bar{1}0]_\delta$ orientation relationship as well as $(111)_\alpha // (110)_\delta$, and the emergence and variations of these ORs between the α and δ phases have been interpreted from the viewpoints of minimum strain.

The phase transformation behavior of the Cu-Sn alloy system with 5–30% Sn is complex because of the similarity of the structures and narrow composition ranges of the phases involved [1, 2]. The β , γ , and δ phases are all based on body centered cubic (bcc) arrangements of Cu and Sn atoms, which are known as electron compounds. When β alloys are relatively slowly quenched, they decompose into a mixture of α and δ phases, displaying a heterogeneous microstructure, which is sometimes called bainite. The present study was initiated to elucidate the crystallography of these heterogeneous reactions in the Cu-Sn alloy at the eutectoid β composition using a focused-ion beam (FIB) technique, which allows local sampling of an area of interest [3]. During the course of the research, however, we realized that the morphology of the nodular bainite in fact resembles that of the as-cast ingot, and the subsequent crystallographic study revealed a striking similarity with a subtle difference.

Figure 1 (a) and (b) are bright field (BF) and dark field (DF) images of a FIB specimen of a nodular bainite region, showing that behind the apparently heterogeneous microstructure, there exists an orientation relationship between the two phases. Figure 1 (c) is a corresponding diffraction pattern obtained along the 110 axis of the δ phase, as well as the 111 axis of the α phase. As seen, two OR, i.e., Nishiyama-Wasserman (NW) and Kurdjumov-Sachs (KS) coexist. The spread of the 220_α spot and the like indicates that there is a spread in the OR.

These variations in ORs between the α and δ phases can be understood by considering: (i) the matching of $(110)_\beta$ (or $(660)_\delta$ and $(111)_\alpha$) spacings, which favors the planes being parallel to each other, (ii) the minimum strain criteria put forward by the invariant line theory for K-S OR, and (iii) the matching of atomic positions in the respective layers in the α and δ phases.

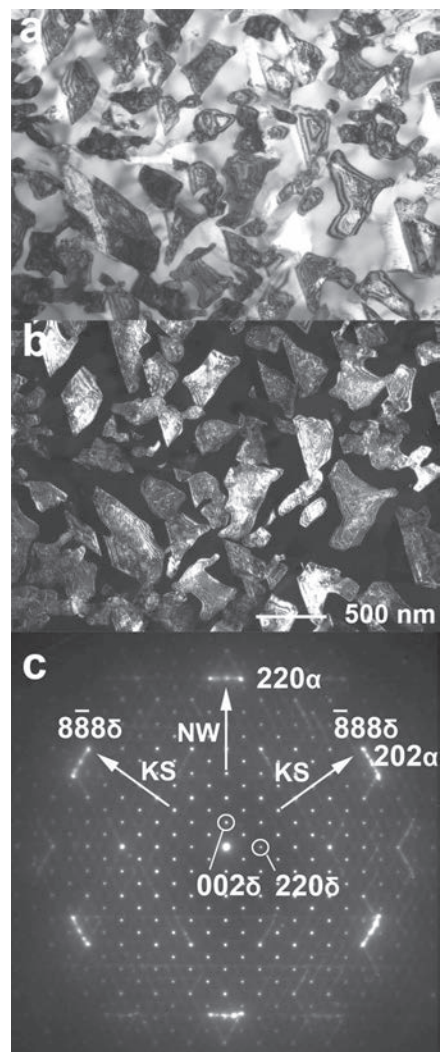


Fig. 1 Microstructure and crystallography of nodular bainite in Cu-Sn alloy (a) BF, (b) DF images, (c) diffraction pattern viewed along the 110 axis of the δ phase, showing the OR between the α and δ phases.

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Keywords: microstructure, metal, transmission electron microscopy (TEM)

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Measurement of Excited Non-Metallic Atoms in Glow Discharge Plasma by Diode Laser Coherent Forward Scattering Spectrometry (DL-CFS)

Excited non-metallic atoms could be sensitively probed by diode laser coherent forward scattering spectrometry (DL-CFS) over the 640–930 nm wavelength range. The signal intensity depended on the 4th power of the number density of argon in the helium plasma. CFS spectrometry was found to be very sensitive to the excitation mechanisms of atoms in glow discharge plasma.

Coherent forward scattering (CFS) spectrometry technique is based on two crossed polarizers, the polarizer and the analyzer, which block the probe light path when there is no atomic interaction. Because of the anisotropy of resonant analyte atoms, which is induced by the applied external magnetic field, the state of light polarization is changed upon passing through the atomic vapor between the polarizer and the analyzer, and light is transmitted. Without light interaction with the resonant atoms, the transmitted intensity is zero. Transmitted CFS intensity is approximately proportional to the square of the number density of atoms. An illustration of this is shown in Fig. 1.

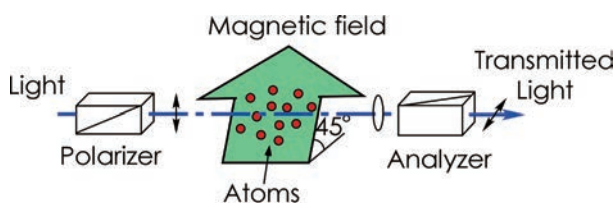


Fig. 1 Illustration of coherent forward scattering spectrometry.

CFS spectra of excited argon atoms, which were produced in a glow discharge plasma, at 842.46 nm were investigated [1]. The CFS signal intensity attained a maximum at 20 mA discharge current at 160 mT external magnetic field in 3 Torr (399 Pa) of argon. Although the lifetime of the lower level of the 842.46 nm line is short (8.4 ns), a relatively strong absorption transition could be observed probably because the population density of the lower level of the 842.46 nm line may be sustained by the electron quenching of argon metastable atoms. A calibration curve of argon was prepared to mix a small amount of argon into 6 Torr (798 Pa) of helium as shown in Fig. 2. The CFS intensity at 842.46 nm depended on the 4.4th power of the number density of argon. This dependence is too large to be explained by the theoretically predicted quadratic dependence.

The dependence may be because of the

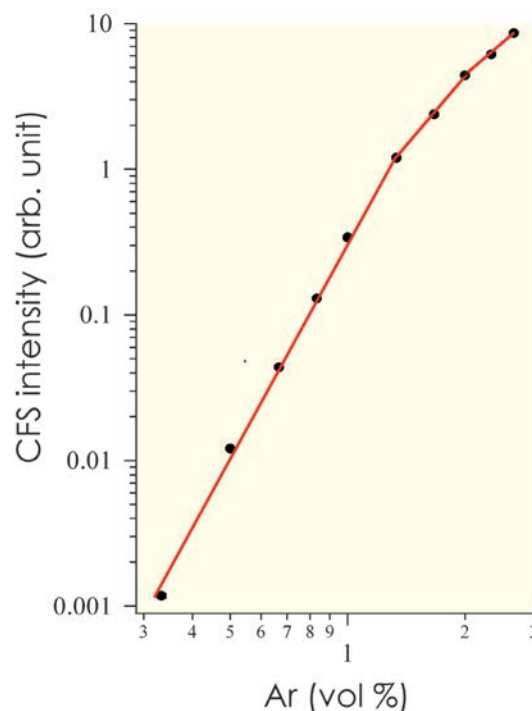


Fig. 2 Calibration curve of admixed argon with helium.

influence of the production processes of argon metastable atoms connecting to the lower level of Ar (I) 842.46 nm. When a small amount of molecular nitrogen was admixed into the argon plasma, a strong suppression of the CFS intensity at 842.46 nm was observed because of the reduction in argon metastable atoms by collisions with molecular nitrogen. Molecular gases such as air were found to be unsuitable to excite target atoms. Noble gases should be used for the plasma gas to produce excited atoms.

CFS spectrometry was found to be very sensitive to the excitation mechanisms of atoms in glow discharge plasma.

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Development of Mg-based Bulk Metallic Glasses for Application as Biodegradable Materials

New Mg-based bulk metallic glasses (BMGs) with high strength and high corrosion resistance have been developed. The corrosion rate and strength can be controlled by a small addition of the element (Ag). Using a spark plasma sintering process, large Mg-based BMGs with high strength and high corrosion resistance have been fabricated, making it possible to use the Mg-based BMGs in biomedical fields.

Bulk metallic glasses (BMGs) have attracted great interest because of their properties such as high mechanical strength, high hardness, high fracture toughness, excellent corrosion resistance, and high wear resistance, compared to conventional crystalline metallic alloys. Many BMG systems have been developed so far. Among them, Mg-based BMGs are of great interest for use as biodegradable implant materials, such as cardiovascular or orthopedic devices. Recently, Mg-based (Mg-Zn-Ca) BMGs have demonstrated a great reduction in hydrogen evolution during in vitro and in vivo degradation [1], showing a potential for application as biomedical materials.

We developed new Mg-based BMGs with high strength and high corrosion resistance. Effects of minor Ag addition on the mechanical properties and corrosion behavior of the Mg-Zn-Ca glassy alloys were investigated. The results reveal that the as-cast Mg-Zn-Ca BMG exhibits a high fracture strength of over 720 MPa. It is further increased with 1 at.% Ag addition, as shown in Fig. 1(a). The corrosion rate in simulated body fluid (SBF) Hanks' solution and strength of the Mg-based BMGs can be controlled by adjusting the Ag content (Fig. 1). The addition of 1 at.% Ag and a homogeneous structure are responsible for improved strength and corrosion resistance. With more Ag addition, the strength of the alloy samples decreases, which originates from a decrease in the glass forming ability of the alloys [2].

It is known that the BMGs are commonly produced using solidification techniques such as copper mold casting. A rather high cooling rate is required to suppress the formation of more thermodynamically stable crystalline phases. Sample size and shape are limited, thereby limiting the range of their applications. On the other hand, it is possible to produce larger metallic glassy alloy parts in a variety of shapes using the consolidation technique [3]. Using a spark plasma sintering (SPS) technique, we developed Mg-based (Mg-Zn-Ca) BMGs and composites in a cylindrical shape with a

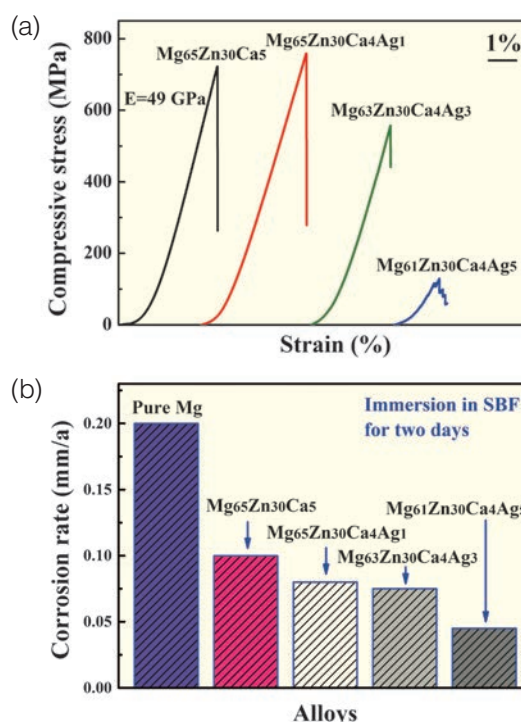


Fig. 1 (a) Compressive stress-strain curves of as-cast Mg-Zn-Ca-Ag alloy rods with a diameter of 2 mm under a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$, (b) corrosion rates of pure Mg and Mg-Zn-Ca-Ag metallic glasses in Hanks' solution.

diameter of over 15 mm [4]. The consolidated Mg-based BMGs exhibited a high strength of over 450 MPa. The corrosion resistance of sintered Mg-based BMGs and the composites was evaluated to be higher than that of pure Mg and commercial AZ31 alloy in Hanks' solution.

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Keywords: metallic glass, powder metallurgy, mechanical properties

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Liquid-solid Phase Transformation Studied through a Large Scale Computer Simulation

Liquid-solid phase transformation is of fundamental importance in controlling the microstructure of engineering materials. Molecular dynamics simulation has been recognized as a powerful tool for analyzing transformation behavior. Introduced below are two recent simulations attempted by key members of CMRI. One is on the solidification process of monolayer colloids by Prof. Terada and the other is the analysis of anisotropy of interfacial velocity for Cu-Al alloy by Dr. Deb Nath. A large-scale computer simulation reveals processes that cannot be readily accessed by ordinary experiments.

Effect of Impurities on the Solidification Process of Monolayer Colloids*

It is important to understand the behavior of impurities on the solidification process for controlling segregation. We constructed a simulation model of the formation of monolayer colloidal crystals from uniform dilute suspensions based on the experiments of an advection accumulation method. By performing a large-scale Brownian dynamics simulation of the solidification process of monolayer colloids with the addition of differently sized impurities, we discussed the effect of size difference between normal colloids and impurities. We found that big impurities induce defects in the crystal region, and they move from more dense regions to less dense regions near the interfaces [1]. Thus, the fraction of big impurities in the crystal region is smaller than that in the initial suspensions.

Melting, Solid-Liquid Interfacial Velocity of Cu-Al Alloys**

Cu-Al alloys are widely used in many industrial applications; but details of the solid-liquid interfacial properties of these alloys are still unknown. Here, we evaluate the melting point and solid-liquid interface velocity of Cu-Al alloys using molecular dynamics simulations. The obtained melting point of Cu-Al alloys will be compared with the experimental results to verify the present simulation results. Deb Nath and his co-authors [2] presented an outline of the molecular dynamics simulation to estimate the solid-liquid interfacial properties of Cu-Al alloys. Figure 2 illustrates the snapshot of solid-liquid interface movement at step 200,000 when Cu₅₀Al₅₀ is heated above the melting point. The anisotropy of the solid-liquid interfacial velocity above and below the melting point is observed, as shown in Fig. 3.

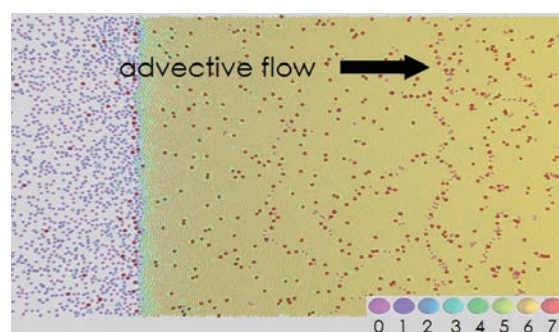


Fig. 1 Picture of 98% normal colloids with radius a and 2% big impurities with radius $1.5a$ at the late stage of solidification process. Each color of the normal colloid indicates the number of nearest neighbor colloids. Dark red particles indicate a large impurity.

Solid-liquid interface

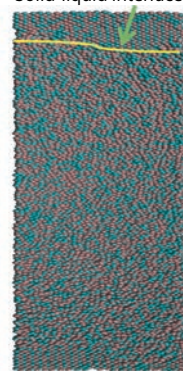


Fig. 2 Picture of Cu₅₀Al₅₀ at step 200,000.

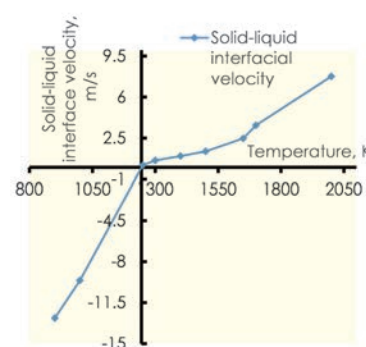


Fig. 3 Solid-liquid interfacial velocity of Cu₅₀Al₅₀.

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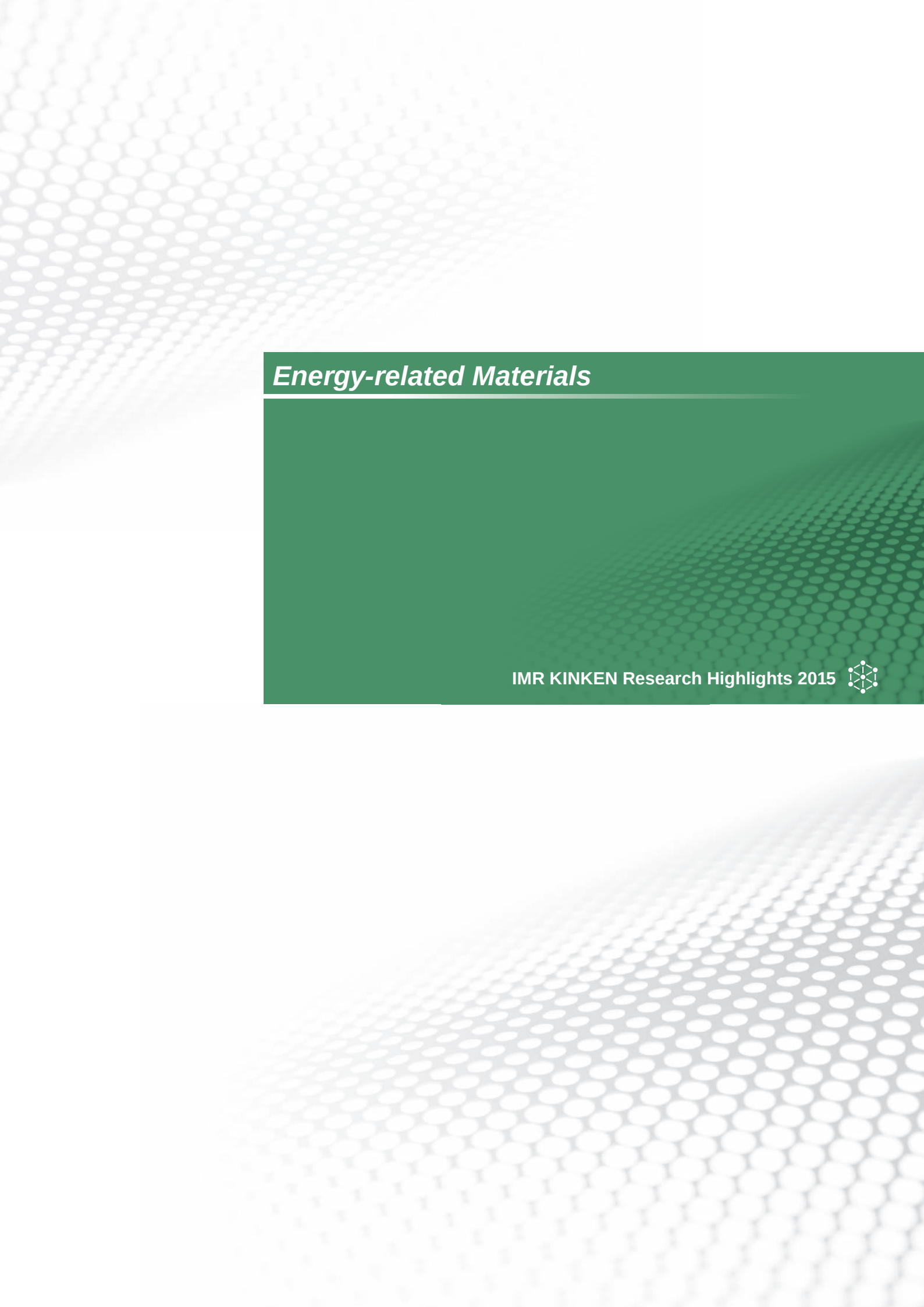
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Keywords: simulation, phase transformation, interface

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Energy-related Materials

IMR KINKEN Research Highlights 2015



Magnon Interactions Modifying Spin Currents

The spin Seebeck effect (SSE) causes spin currents to flow in an insulator when a thermal gradient is applied. Simple theories can describe this effect, but it is not well known how the spin is generated and transported in complicated ferrimagnetic garnets. The spin wave modes present in these materials can contribute to the SSE. Using detailed numerical calculations, we are beginning to understand the important role played by spin waves in the ferromagnetic order of these materials.

The spin Seebeck effect [1] is typically observed in ferrimagnetic insulators, such as yttrium iron garnet (YIG); however, other materials, such as gadolinium iron garnet (GdIG), are also being explored. A temperature gradient across the insulator pumps a net spin current into an attached metal such as Pt. This effect has potential uses in spintronics and energy scavenging, but more material-specific understanding is required to fully exploit this.

Recent experiments conducted in Munich, Mainz, and Sendai revealed that the SSE changes sign twice in the GdIG | Pt system; once at the magnetization compensation temperature and a second time at a lower temperature where there are no significant changes in the macroscopic magnetic properties.

Using numerical simulations based on detailed atomistic spin models, we studied how the spin wave spectra of YIG and GdIG change with temperature; this was done to better understand the role of magnon interactions in the thermally induced transport of spin current. We found that the polarization of the spin wave modes determines the sign of the contribution to the SSE. The frequency and amplitude of the spin wave modes change with temperature.

The many-body nature of the numerical approach provides information about dispersion and amplitude of all spin wave modes. Most of them broaden but remain almost stationary in frequency as the temperature is increased. However, we observe in Fig. 1 that one optical mode is significantly red-shifted and the magnon gap at 2 THz increasingly closes with increasing temperature. The amplitude of this mode also increases, giving rise to an increasing contribution to the SSE with opposite sign compared to that of the lowest ferromagnetic magnon band. In GdIG, this leads to the observed second sign change.

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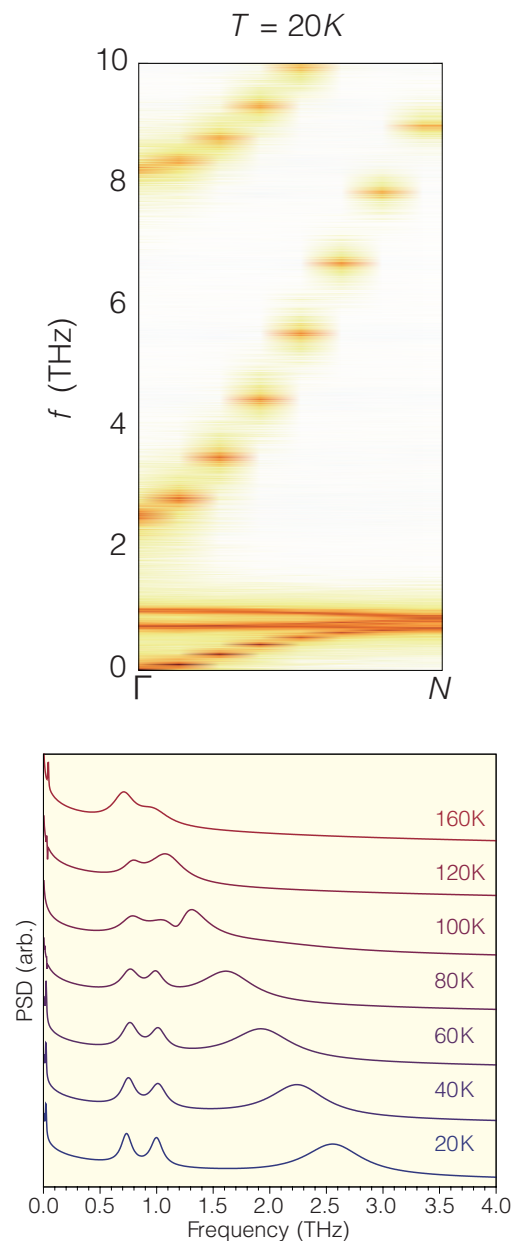


Fig. 1 (top) Low-frequency part of the GdIG spin wave spectrum. The magnon-gap at 2 THz is caused by the presence of the Gd. (bottom) Line scan at $k = 0$ shows that this gap reduces with increasing temperature.

Keywords: spintronics, insulator, spin wave

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Cu Precipitation Conditions at Small Angle Tilt Boundaries in Si

Impurity gettering at grain boundaries plays a decisive role in determining macroscopic properties of most polycrystalline materials, as well as in fabricating stable nanostructures. We have recently shown the Cu precipitation conditions at small-angle tilt boundaries (SATBs) in Si crystals depending on Cu contamination levels, which are similar to the Cu precipitation conditions in metallic alloys. Here, we highlight the nanoscopic mechanism of the Cu precipitation, which may be universal in non-insulating polycrystalline materials with metallic impurities.

Impurity gettering at grain boundaries in Si crystals influences the photovoltaic properties of solar cells fabricated with polycrystalline Si. Accordingly, a comprehensive knowledge of impurity gettering conditions is essential for engineering size and spatial distributions of impurity-related nanostructures at grain boundaries in a controlled manner in order to produce cost-effective functional solar cells.

Here, we determined the Cu precipitation conditions at small-angle tilt boundaries (SATBs) on (220) in a Czochralski-grown p-type Si crystal [1] by high-resolution transmission electron microscopy (HRTEM) and ab-initio calculations [2] combined with atom probe tomography (APT) [3]. The Cu precipitation process was explained in terms of the balance of the precipitation and interface energies for the precipitates as well as the strain energy due to lattice mismatch and edge dislocations in the SATBs (EDLs). During the initial stage of precipitation, Cu atoms agglomerated along SATBs forming coherent layers of Cu_3Si with a body-centered cubic structure in a meta-stable state ($a = 0.285 \text{ nm}$) (Fig. 1). As the layers thickened, they became semi-coherent layers with misfit dislocations on the (220) interphase boundaries to reduce coherency strains (Fig. 2). Subsequently, as Cu atoms agglomerated further, the metastable layers converted into incoherent polyhedrons of orthorhombic $\eta''\text{-Cu}_3\text{Si}$ in the thermal equilibrium state, forming interphase boundaries on {112} in Si (Fig. 3).

The Cu precipitation process observed in Si appears to be similar to that in metallic alloys; the formation of Guinier-Preston (GP) zones followed by conversion into the equilibrium θ -phase. The precipitation process may be universal in non-insulating polycrystalline materials with metallic impurities. Our finding can provide a general guide to control Cu contaminants in polycrystalline Si, which will enable lower-quality Si feedstock to be fabricated into cost-effective functional solar cells. In addition, it has potential applications in Cu-Si interface nanotechnologies such as nanoscale field-emitters and interconnects.

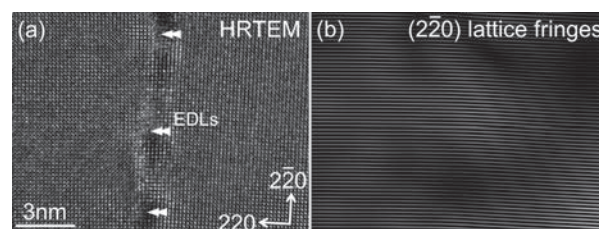


Fig. 1 (a) HRTEM of a coherent bcc- Cu_3Si layer at a SATB in an as-grown Si. (b) Lattice fringes of (220) in (a).

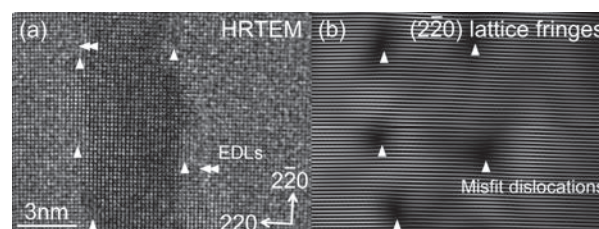


Fig. 2 (a) HRTEM of a semi-coherent bcc- Cu_3Si layer at a SATB in an annealed Si. (b) Lattice fringes of (220) in (a).

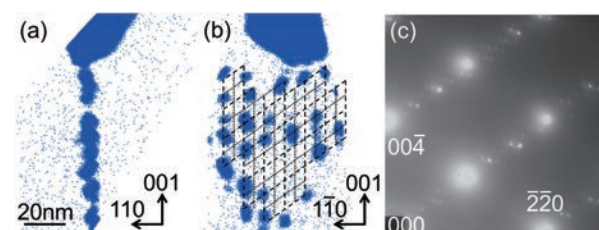


Fig. 3 Projected 3D distribution of incoherent polyhedrons of orthorhombic $\eta''\text{-Cu}_3\text{Si}$ at a SATB in an annealed Si viewed (a) parallel to and (b) normal to the SATB. (c) Diffraction pattern of the polyhedrons for $[2\bar{2}0]$ incidence.

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Multiphysics Simulation Based on Quantum Chemical Molecular Dynamics Method

Recent material and system technologies constitute of multiphysics phenomena including chemical reaction, friction, impact, stress, fluid, photon, electron, heat, electric field etc. and then a deep understanding of the above multiphysics phenomena is strongly required. Therefore, we have pioneered multiphysics simulation technologies based on our quantum chemical molecular dynamics method.

To solve current energy and environmental problems, high-functional and high-performance materials are highly demanded in a wide variety of research fields, such as tribology, aerospace instruments, fuel cell, solar cell, micromachine, etc. In particular, recent material and system technologies constitute of multiphysics phenomena including chemical reaction, friction, impact, stress, fluid, photon, electron, heat, electric field etc. and then a deep understanding of the above multiphysics phenomena is strongly required. However, traditional simulation methods, such as first-principles calculations and fluid mechanics, cannot simulate the above multiphysics phenomena. Therefore, we have developed new multiphysics computational simulation technologies based on our quantum chemical molecular dynamics method for pioneering next-generation material design [1-3].

Diamond-like carbon (DLC) is expected to be used as a solid lubricant. Thus, to design low-friction DLC films, we investigated the effects of H- and F-termination on the friction behavior of DLC films [1]. Figure 1 shows that the friction coefficients for the H-terminated DLC (H-DLC) and F-terminated DLC (F-DLC) films are 0.38 and 0.10, respectively, under a high contact pressure of 7 GPa. Moreover, we found that C–C bond formation during friction causes the friction coefficient of the H-DLC film to be higher than that of the F-DLC film and the strong repulsive interaction between the F atoms is the reason for less C-C bond formation of the F-DLC film than that of the H-DLC film. Thus, we suggest that F-termination improves the friction properties of DLC films.

Thin-film Si is expected to be a next-generation solar cell. The surface smoothening during the chemical vapor deposition (CVD) process is key for its performance. Therefore, we performed Si CVD simulations and proposed a dangling bond (DB) diffusion model as an alternative to the SiH₃ diffusion model, which does not match the experiments. In our model, the DBs diffuse rapidly along an upper layer consisting of Si-H₃ sites and then migrate from the

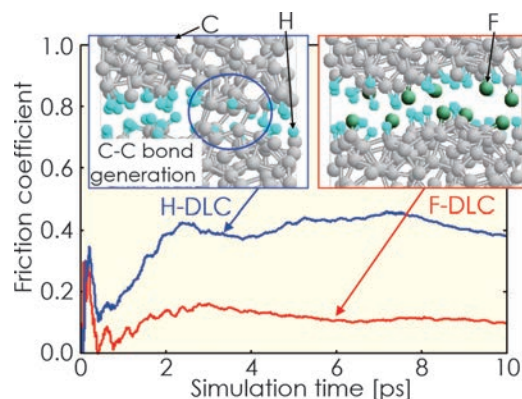


Fig. 1 Friction coefficients for H- and F-DLC films under a pressure of 7 GPa.

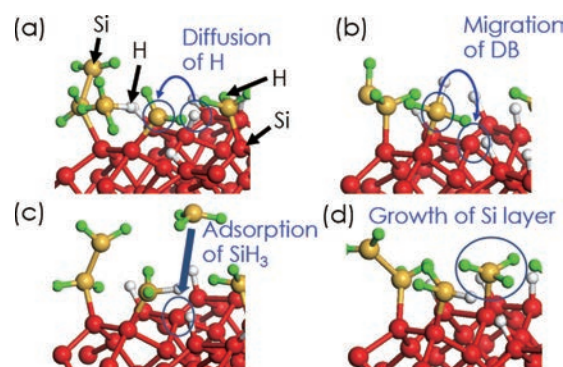


Fig. 2 Snapshots of Si CVD simulation at (a) 35 ps, (b) 36 ps, (c) 39 ps, and (d) 40 ps.

upper layer to a lower layer consisting of Si-H sites. The subsequently incident SiH₃ radical is then adsorbed onto the DB in the lower layer, causing two-dimensional growth. Our findings can explain the reason why the layer-by-layer growth occurs [2].

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Effects of Ion Implantation on Hydrogen and Helium in SiC for Fusion Applications

The retention/release behavior of H isotopes and He is important in controlled fusion devices. We found a significant accumulation of hydrogen in a damaged layer upon air exposure after completion of the thermal release of He implanted in SiC single crystals.

Silicon carbide (SiC) is a promising material for components such as first wall, tritium breeding blankets, and insulating materials, in nuclear fusion reactors owing to its inherent properties, such as low activation, good thermal conductivity, and stability at high temperatures. As a first wall material, SiC is subjected to severe high-energy neutrons and energetic He bombardment from the plasma. The retention of tritium in breeding materials is a critical issue from the viewpoint of tritium recycling [1]. We investigated the ion irradiation effects and the interactions between H and He in SiC crystals using the elastic recoil detection analysis [2].

The depth profiling during isochronal annealing experiments showed that the D retention in He⁺ implanted SiC at 1370 K was smaller than that for D implanted into the un-irradiated SiC crystal. The reduction in D retention at 1370 K can be explained by He implantation-induced damage, which suppressed the formation of C–D bonds. Besides, the morphological changes during thermal release of He may contribute to accelerate the recombination process of D atoms. A significant increase in He release temperature was found in the D₂⁺ implanted SiC, indicating suppression of He bubble formation by D remaining in SiC at high temperature. The damage induced by He and D implantation was not recovered from the saturating concentration even at 1370 K. The release behavior of ion-implanted D and He has no relevance to the annealing behavior of the implantation-induced disordered layer observed by Rutherford backscattering combined with the ion channeling technique. The H atoms were accumulated in the damaged layer upon air exposure after completion of the thermal release of He in a vacuum, probably due to the dissociation of water molecules at the surface. However, H was not observed in the D implanted SiC even after D was released.

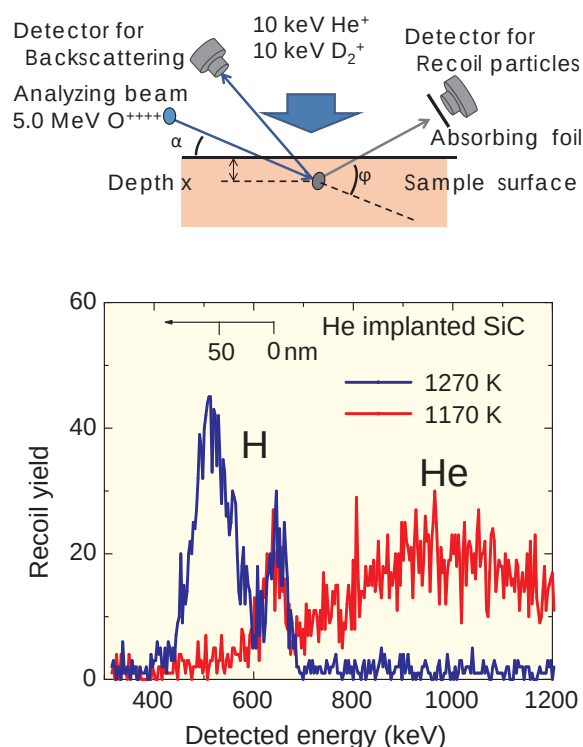


Fig. 1 (Top) Schematic illustration of H and He detection using the ion beam. (Bottom) Recoil spectra from He implanted SiC after annealing at 1170 and 1270 K for 10 min in vacuum.

For the implantation at 770 K, the D retention and D-ion-induced disorder were drastically decreased compared with implantation at 300 K. The He pre-implantation induced damage did not influence the D retention at 770 K, while the He-ion-induced displacements were considerably larger than those induced by the D implantation alone.

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Keywords: hydrogen implantation, ion beam analysis, nuclear materials

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Development of an Advanced Expansion due to Compression (A-EDC) Test Method for Safety Evaluation of Nuclear Fuel Cladding

The expansion due to compression (EDC) test was modified to evaluate the performance of tubular materials like nuclear fuel claddings where pellet-cladding mechanical interaction (PCMI) triggers the larger hoop deformation of the pellets, particularly during accidental transients. The purpose of this study is to modify the EDC test by specimen volume reduction and other methods to overcome its shortages and disadvantages. Using ring-shaped specimens and cylindrical metal pellets as the inner pellets, expansion of the specimens due to the inner pellet compression was performed. Together with the analysis using the finite element method, the experimental set-up was optimized. The ideal uniaxial tension condition in the hoop direction up to the failure, as well as excellent reproducibility with less error, was confirmed. Stress–strain curves in the hoop direction were successfully derived.

Tubular materials like nuclear fuel cladding are generally required to maintain their mechanical strength during exposure to an environment where corrosion, hydrogenation, and/or irradiation damage are present [1]. In the case of nuclear fuel claddings, an increase in the stress and strain in the hoop (circumferential) direction is caused by an increase in the inner pressure because of accumulation of fission product gas in the gap between the fuel pellet and the cladding, pellet-cladding mechanical interaction (PCMI) by swelling of fuel pellets, and the resulting bonding. Though the EDC and other tests have been applied to evaluate the material performance, shortages and disadvantages were pointed out, such as limitation of the test temperature and limitation in post irradiation experiments arising from the radioactivity. The purpose of this study is, therefore, to modify the EDC test to describe PCMI, specimen volume reduction, and others [2].

Ring-shaped specimens were cut from Zry-4 cladding tubes. Cylindrical metal pellets 8 mm in diameter and 15 mm in maximum height were used as inner pellets. Expansion of the specimens because of inner pellet compression was performed at room temperature. The experimental data were further analyzed by the finite element method. Through a survey of the variation of the specimen and inner pellets, the geometry of the specimens and inner pellets were optimized. Excellent reproducibility with less error was confirmed. The uniaxial tension condition in the hoop direction up to specimen failure was confirmed. Hoop stress–hoop strain curves were successfully derived.

In this work, the problems of the conventional EDC test were elucidated, and an advanced EDC (A-EDC) test was developed. Employing metallic inner pellets and ring-shaped specimens, a great reduction in the sample volume was achieved. Reduction in radioactivity is expected in material test reactors or accelerator irradiation experiments and post-irradiation experiments

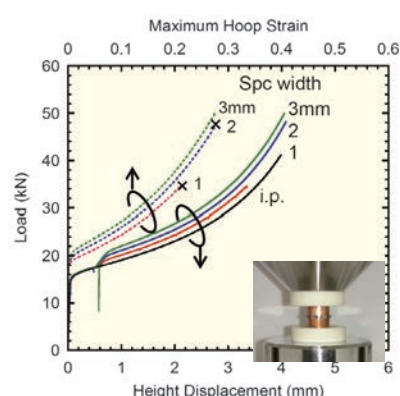


Fig. 1 Load-displacement curves of A-EDC test. Inset shows the experimental setup.



Fig. 2 Hoop stress and hoop strain curves in Cu inner pellets with 1 and 2 mm specimen width.

under varied environmental conditions. Using experiments and FEM simulations, ideal uniaxial hoop tension up to the fracture of specimen, with better reproducibility and less error, was confirmed.

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Keywords: nuclear materials, mechanical properties, zirconium alloy

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High-efficiency N-polar InGaN/GaN Solar Cells with Promotion of Photocarrier Extraction by Polarization Fields

N-polar nitride-based devices have a strong electric field due to both spontaneous polarization and piezoelectric polarizations. In a p-i-n structure of solar cells, this field is applied along the same direction as the built-in field, and is expected to enhance the extraction of photo-carriers. We have demonstrated N-polar InGaN/GaN solar cells for the first time and confirmed this effect.

The nitride semiconductors InGaAlN are promising materials not only for light-emitting devices, but also for high-efficiency solar cells because their band-gap can encompass the entire solar spectrum. In nitride semiconductors with a wurtzite crystal structure, a strong polarization is generated along the $\langle 0001 \rangle$ axis as shown in Fig. 1. By adopting the nitrogen polar (000 $\bar{1}$) plane during growth for fabricating solar cells, the polarization field can be incorporated in the built-in field, which drives photo-carriers to the metal electrodes in a conventional solar cell with a p-i-n structure. These polarization fields are expected to improve the conversion-efficiency. For this purpose, the technique for N-polar growth is extremely useful. However, all the devices developed until now and available commercially use Ga-polarity. We have already reported N-polar growth with a smooth surface [1, 2] and p-type conduction [3] by metalorganic vapor phase epitaxy (MOVPE). In addition, we have succeeded in the fabrication of LEDs with InGaN/GaN multiple quantum wells (MQWs) from red to blue colors [4]. In this paper, an N-polar solar cell fabricated on a sapphire substrate is described. Their characteristics are also shown and compared to the Ga-polar cells.

The N-polar solar cell consists of undoped GaN, Si-doped n-type GaN, InGaN/GaN MQWs, and p-type GaN, which is the same as a conventional GaN-based light-emitting diode.

The current- and the power-density versus voltage characteristics were evaluated under 1 sun of the AM1.5 equivalent illumination. The N-polar InGaN/GaN solar cell operation was demonstrated for the first time. The open-circuit voltage and the short-circuit current density were 0.85 V and 62.4 $\mu\text{A}/\text{cm}^2$, respectively. The bias-dependent spectral responses are shown in Fig. 2. For the Ga-polar solar cell, the photocurrent strongly depended on the bias voltage. This indicates that both the built-in field and the polarization field are not effective for the extraction of photo-carriers. For the N-polar solar cell, the photocurrent does not depend on the bias voltage and both fields can be considered to effectively play a role in the extraction of photo-carriers.

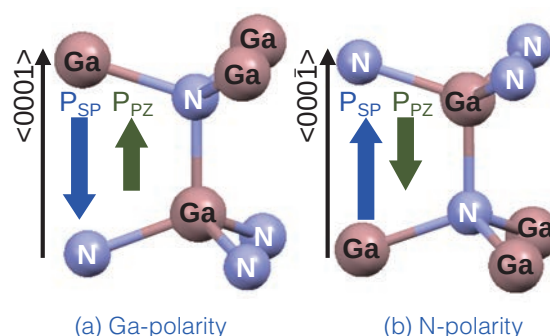


Fig. 1 Atomic arrangements and direction of spontaneous (P_{sp}) and piezoelectric (P_{pz}) polarization for GaN under compressive strain.

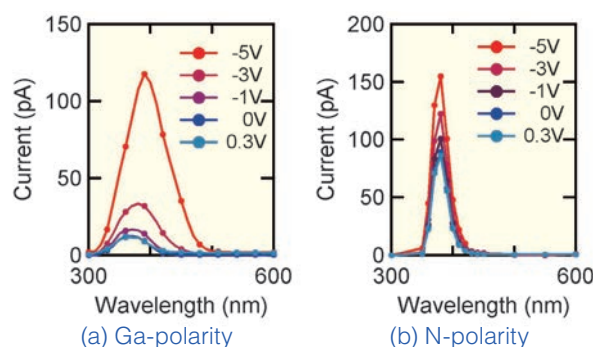


Fig. 2 Bias-dependent spectral response for InGaN/GaN solar cells with different crystallographic polarity.

In conclusion, N-polar solar cells have the potential to achieve high-efficiency solar cells.

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Keywords: nitride, solar cells, vapor phase epitaxy (VPE)
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Bulk Nanoporous Silicon Negative Electrode with Extremely High Cyclability for Lithium-Ion Batteries Prepared Using a Top-Down Process

A top-down process utilizing dealloying in a metallic melt was used to obtain freestanding three-dimensional nanoporous bulk Si. We fabricated a high capacity negative electrode (capacity approaching the theoretical limit) for lithium ion battery with nanoporous Si. Compared to conventional electrodes made from Si nanoparticles, our electrode material greatly extended the lifetime, and significantly improved the battery performance. Nanoporous structures that are capable of accommodating large changes in volume during charging are responsible for the prolonged lifetime cycle and superior performance.

Si is a promising active material as the negative electrode of Li-ion batteries (LIBs) because it has a theoretical Li capacity of ~ 4200 mAh/g, approximately 10 times that of carbon-based electrodes. However, Si electrodes suffer from volume changes of more than 400% with Li insertion and removal. This large volume change pulverizes the conductive network between the active material and the current collector, rapidly degrading the cyclic performance. Many researchers have studied ways to accommodate this volume change by using nanostructured Si including thin films, nanotubes, nanowires, and nanoporous structures. The nanoporous Si-based negative electrodes exhibited improved cyclic performance because the many open channels in such structures act as ideal volume expansion buffers. Despite such promising performance of the nanoporous Si-based electrodes, the preparation has generally required several complicated steps, such as fabricating a template for deposition of material, making the preparation expensive, slow, and difficult to scale up. To overcome these issues, we originally developed dealloying in a metallic melt [1, 2], a simple top-down process for fabricating nanoporous Si.

We synthesized freestanding 3D nanoporous Si by immersing a precursor of Mg_2Si intermetallic compound in a pure Bi melt at 1123 K. Because the Mg is miscible in Bi but Si is not, the Mg atoms in the precursor selectively dissolved into the Bi melt, and the remaining unstabilized Si atoms spontaneously organized into a 3D nanoporous structure with average pore size and porosity of 400 nm and 60.4%, respectively, as shown in Fig.1.

Using this nanoporous Si, we fabricated negative electrodes for LIBs. Figure 2(a) shows the cyclic performance of the electrode operated in a constant current (CC) mode. The electrode exhibited almost theoretical capacity (3579 mAh/g), and excellent capacity retention of >2000 mAh/g over 200 cycles, significantly improved compared to electrodes fabricated from a commercial Si nanoparticle. We further improved the performance of the electrodes by controlling the depth of lithiation based on the relation between the volume change and the porosity of nanoporous Si. Figure 2b shows cyclic performance of the electrode operated at a constant charge capacity of 1000 mAh/g, in which the volume change and the pore volume become nearly equal. The capacity of the electrode didn't degrade over

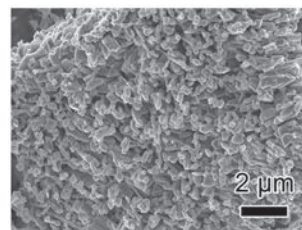


Fig. 1 SEM image of the 3D nanoporous Si prepared by immersing a precursor of Mg_2Si intermetallic compound in a pure Bi melt at 1123 K.

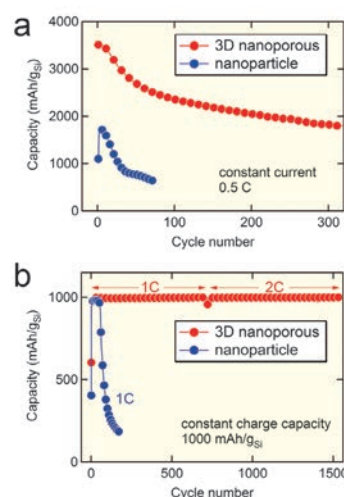


Fig. 2 Cyclic performance of the nanoporous Si electrodes. (a) constant current mode at 0.5 C and (b) constant charge capacity mode at 1000 mAh/g_{Si}. The 1 C rate corresponds to 3579 mA/g_{Si}.

1500 cycles, which is greatly prolonged compared to that operated by CC mode, indicating that the 3D nanoporous structure effectively accommodated volume expansion due to lithiation, which was helpful for improving capacity and life cycle of LIB electrodes.

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Keywords: foam, porosity, energy storage
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Improvement in Crystal Quality of Protein Crystals under an External Electric Field

Crystal quality and crystal homogeneity of protein crystals were improved by application of an external electric field. This method utilizing an external electric field is a novel crystallization technique for proteins, which can be employed not only to enhance the nucleation rate but also to improve the crystal quality.

In order to allow both structure-guided drug design and controlled drug delivery, it is important to determine the 3D structures of protein molecules. At present, these structures are primarily determined using X-ray diffraction (XRD) analysis, and therefore, high-quality single crystals of proteins are required, even though these are quite difficult to obtain. Thus, the establishment of a crystallization technique that can provide high-quality single crystals of proteins is required.

Previously, we have concentrated on controlling the nucleation rate of proteins by applying an external electric field. Consequently, the control of both the increase and the decrease in nucleation rate for proteins was successfully achieved under application of an electric field by focusing on the chemical potentials of the liquid and solid [1,2]. Therefore, if crystal quality could also be improved by application of an external electric field, then, this crystallization technique could be an excellent tool.

Figure 1 shows the two-dimensional maps of the full width at half maximum (FWHM) measured for the 440 and the 12 12 0 reflections from tetragonal hen egg white (HEW) lysozyme crystals prepared with and without an external electric field. As shown in Fig. 1, it was found that the values of FWHM with an external electric field at 1 MHz were smaller than

those without an external field [3], and the overall crystal quality was homogeneous for the crystals prepared with an external electric field [4]. This suggests that the crystal quality and crystal homogeneity of protein crystals can be improved by the application of the external electric field at 1 MHz. Moreover, from the FWHM analysis of the rocking curves, it was determined that improvements in the quality of tetragonal HEW lysozyme crystals are attributed to a decrease in the misorientation between subgrains in the crystal during crystal growth [5]. This crystallization technique is expected to enhance the resolution of protein molecular structure analysis by X-ray diffraction.

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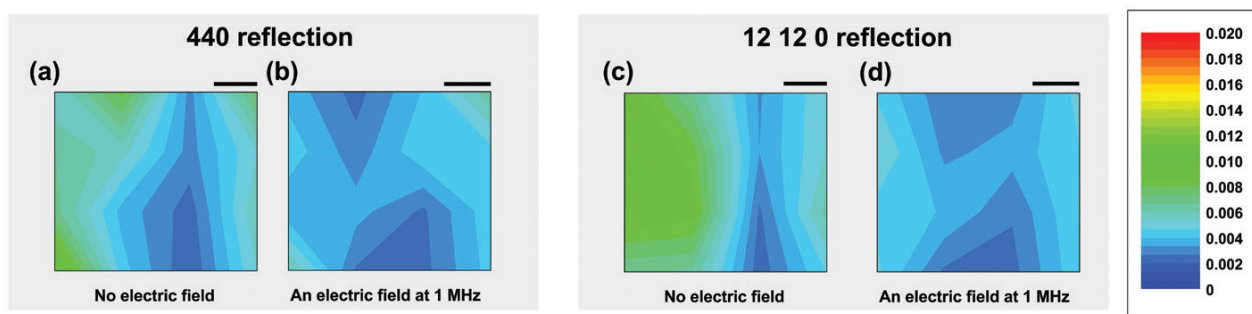


Fig. 1 Two-dimensional maps of FWHMs measured for the 440 and the 12 12 0 reflections from tetragonal HEW lysozyme crystals prepared with and without an external electric field. (a) and (c) No electric field, and (b) and (d) applied fields at 1 MHz. The upper-right scale bar for each two-dimensional map represents 0.3 mm.

Keywords: crystal growth, X-ray diffraction (XRD), biological
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Hydrogen Storage Materials with Optimal Thermodynamic Stability

Among the methods spanning many approaches, solid-state hydrogen storage using complex transition-metal hydrides as a storage medium has a clear advantage in weight and volume efficiencies. The major disadvantage is the high thermodynamic stability that makes reversible room temperature applications difficult. Here, we present a strategy for designing complex hydrides with thermodynamic stability suitable for hydrogen storage.

Dimagnesium iron(II) hydride (Mg_2FeH_6 , left panel in Fig. 1) is a prototypical member of a family of complex transition-metal hydrides, where covalent Fe–H interactions in a tetravalent $[\text{FeH}_6]^{4-}$ anion are stabilized by charge transfer from two divalent Mg^{2+} cations. While this material reversibly stores a large amount of hydrogen, the relatively high thermodynamic stability makes room temperature hydrogen storage applications challenging. In this regard, we recently reported a linear relationship between the standard heat of formation and cation electronegativity for the $(M,M')_2\text{FeH}_6$ system; *i.e.*, the thermodynamic stability can be tuned by substituting Mg with elements of different electronegativity [1]. While this relationship provides a useful insight into the rational design of new complex hydrides, the tunability of thermodynamic stability is practically limited to some extent because of a small number of possible combinations of cations to compensate the tetravalent charge state of the $[\text{FeH}_6]^{4-}$ anion. One strategy for increasing these combinations is to raise the total anionic charged state. To this end, here we introduce a novel method for increasing the charge state by incorporating H^- anions in complex hydrides, as shown in the right panel in Fig. 1 [2].

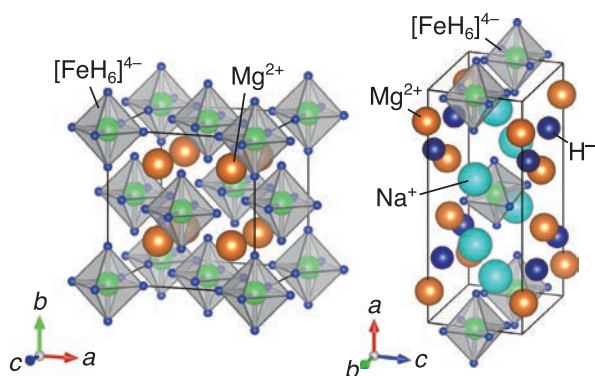


Fig. 1 Crystal structures of Mg_2FeH_6 (left), and $\text{Na}_2\text{Mg}_2\text{FeH}_8$ containing two H^- ions (right).

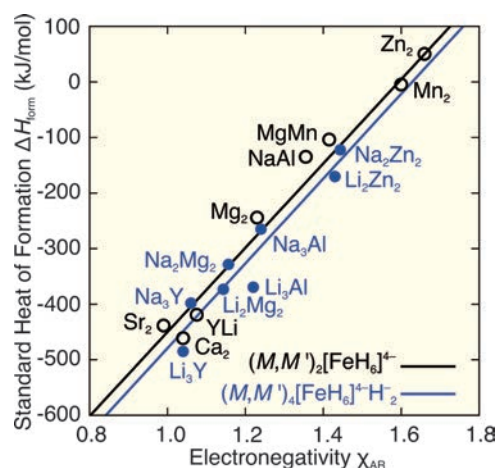


Fig. 2 Standard heat of formation as a function of cation electronegativity for the complex hydrides $(M,M')_2[\text{FeH}_6]^{4-}$ (black open circle) and $(M,M')_4[\text{FeH}_6]^{4-}\text{H}_2$ (blue solid circle). The values were taken from Ref. 1 and 2.

Figure 2 shows the standard heat of formation of $(M,M')_4\text{FeH}_8$, composed of an $[\text{FeH}_6]^{4-}$ anion, two additional H^- ions, and a total of four cations that compensate the hexavalent anionic charge state, as a function of cation electronegativity. As is evident from the blue solid circles, a linear relation can be seen between the heat of formation and cation electronegativity as well as the $(M,M')_2\text{FeH}_6$ system without the incorporation of H^- ions. Thus, the chemical flexibility provided by incorporating H^- ions enhances the tunability of thermodynamic stability, which will be beneficial in obtaining materials with optimal stability for reversible room temperature hydrogen storage.

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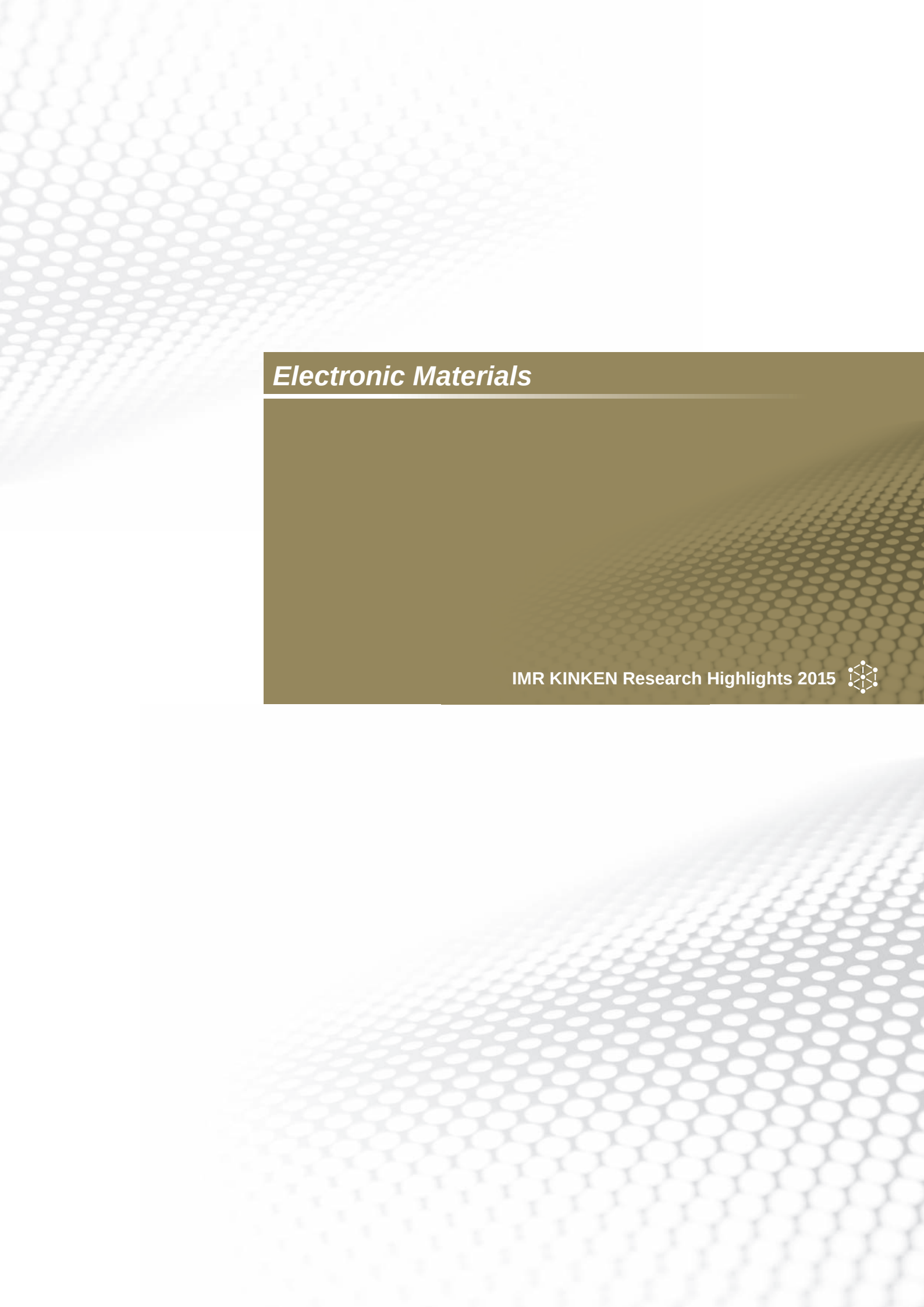
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Keywords: hydride, electronic structure, first-principles calculations

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Electronic Materials

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Giant Artificial Spin on a Molecule-Ferromagnetic Cage Cluster Fe₄₂

The ferromagnetic ground state of a molecular cluster showing $S = 45$ high spin state is found by low-temperature magnetization, X-ray spectroscopy, and high-frequency EPR. This is the largest artificial spin found ever. The ferromagnetic coupling is mediated by the highly symmetric network of the mixed-valence Fe ions.

Synthesis of new giant spins on single molecular clusters is one of the most important fields of magnetism. Such ferromagnetic molecular clusters are essential for realizing ultra-high density molecular storage and/or quantum spin devices. Coordination bonds among magnetic ions mediated by anions are, in many cases, antiferromagnetic. This makes the creation of a high-spin ground state challenging. A possible approach is to use rare-earth elements that have large magnetic moments. However, use of ubiquitous elements such as Fe³⁺ $S = 5/2$ is desired, for environmental safety.

The present material contains 42 Fe ions, 18 of which are in Fe³⁺ $S = 5/2$ states. To align these high spins into a ferromagnetic cluster, the charge and the spin states of the Fe ions are tuned [1]. As a result, ferromagnetic coupling arises for the interactions between mixed-valence Fe ions. The high symmetry of the cluster is another key point of the ferromagnetic ground state as a whole cluster. The synthesis was made in the Sato group at the Institute for Materials Chemistry and Engineering, Kyushu University. The material was then transferred to the Magnetism division of the Institute for Materials Research for further physical analysis.

Figure 1 depicts the magnetization curve measured at 0.5 K, which shows a steep increase in low magnetic fields and saturation at 90 μ_B ($S = 45$, $g = 2$). This is the fingerprint of the ferromagnetic ground state. In many ferromagnetic molecular clusters, bulk ferromagnetic ordering takes place. The possibility of such ferromagnetic ordering must be excluded to establish that the ferromagnetic ground state is realized on an isolated single molecule. The first evidence is the temperature and magnetic field dependence of the magnetization showing no critical temperature. The second evidence is the absence of an anomaly related to magnetic phase transitions by means of calorimetry.

Another characteristic of this Fe₄₂ cluster is very small hysteresis. High frequency EPR reveals that the anisotropy is very small in this compound though highly anisotropic Fe²⁺ ions are involved. This

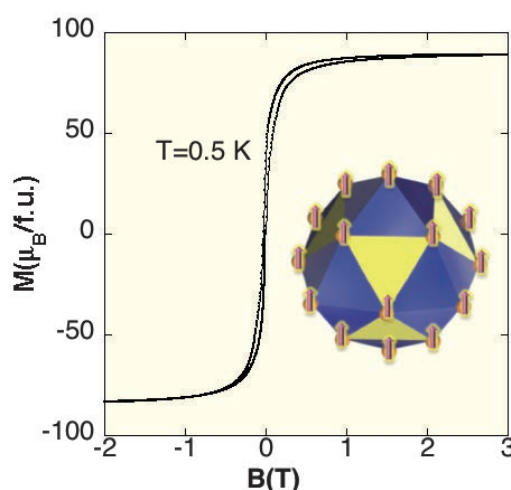


Fig. 1 The magnetization curve measured at 0.5 K, which shows the steep increase in low magnetic fields and the saturation at 90 μ_B ($S = 45$, $g = 2$). The inset shows the shape of the molecule with high symmetry.

isotropic nature is caused by the cancellation of the local anisotropies for the highly symmetric cluster shape. The symmetry of the cluster is shown in the inset of Fig. 1. The network has a star-like side view, and the crystal has a highly symmetric cubic lattice.

Finally, the differentiation of the magnetic moments and the charge states of the complex mixed-valence network is made using X-ray spectroscopy at SPring8. The obtained ratio among four different states containing Fe²⁺/Fe³⁺ and high/low spin states is consistent with the ferromagnetic ground state.

These intensive studies using different probes finally establish the giant spin ground state of the Fe₄₂ cluster. Possible photo-control of electron transfer to modify the spin ground state is in progress.

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Topological Insulators as Inborn Spintronics Devices

Detection and manipulation of electron spins are key prerequisites for spintronics. Since spin currents decay on a length scale less than a few micrometers, thin-film nanostructures have been indispensable in spintronics devices. Here, we experimentally demonstrate that, contrary to this limitation, a bulk topological insulator acts as a spin detector without forming into films.

A topological insulator is a new state of quantum matter that possesses a surface metallic state and an insulating interior. This characteristic of topological insulators is the structure commonly used in spintronics, *i.e.*, a conductor film artificially made on an insulator substrate. Furthermore, conduction electrons on the surface state are helical Dirac fermions that have a novel property called spin–momentum locking. On the surface states of topological insulators, the direction of the electron motion determines its spin direction and vice versa. Hence, if a spin imbalance is induced by the spin injection, a charge current is expected to be produced along the Hall direction, as illustrated in Fig. 1.

By exploiting these features combined with spin pumping, we experimentally demonstrate spin–electricity conversion in a bulk topological insulator $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.7}\text{Se}_{1.3}$ (BSTS), where injected spins are converted into electric voltage along the Hall direction despite the bulk nature of the samples [1]. Figure 1 shows the results of the electromotive-force measurement with a magnetic field at various temperatures for $\text{BSTS}/\text{Ni}_{81}\text{Fe}_{19}$. At ferromagnetic resonance of $\text{Ni}_{81}\text{Fe}_{19}$, voltage peaks whose signs are odd with respect to external magnetic fields are observed. This sign reversal of the voltage signals is consistent with the spin–electricity conversion induced by spin–momentum locking on the surface states of topological insulators.

The physical origin of the observed spin–electricity conversion effect is the spin–momentum locking. This mechanism is fundamentally new, because there is no flow of injected spins in topological insulators, unlike in conventional materials. Moreover, because of the one-to-one correspondence between spin and momentum directions, 100% spin–electricity conversion is, in principle, possible for topological insulators. The present results reveal a great advantage of topological insulators as inborn spintronics detectors.

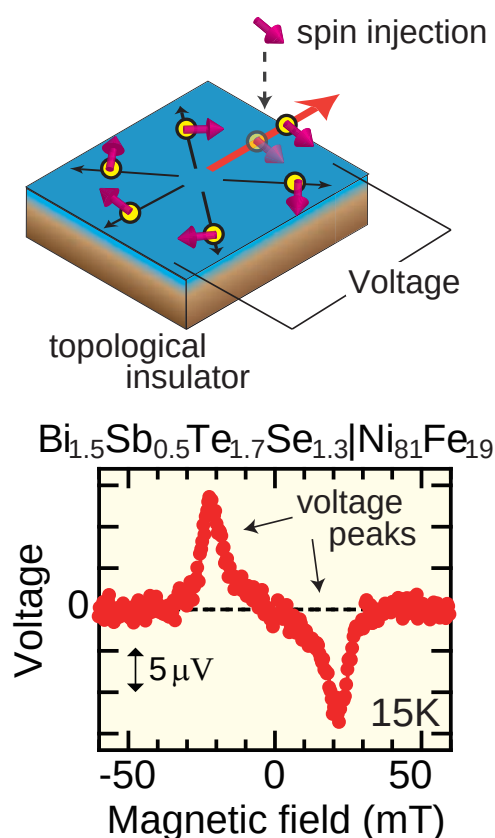


Fig. 1 (top) Concept of spin–electricity conversion on surface states of topological insulators. (bottom) Electromotive force for $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.7}\text{Se}_{1.3}$ (BSTS) attached with a $\text{Ni}_{81}\text{Fe}_{19}$ film at 15 K. Clear antisymmetric voltage peaks are observed on the surface state at ferromagnetic resonance of $\text{Ni}_{81}\text{Fe}_{19}$.

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Keywords: spintronics, electronic material, spin current
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Tuning the threshold voltage of a polar-semiconductor field-effect transistor

Polar-semiconductor heterostructures host two-dimensional electron accumulation, which can be applied as a conducting channel in a high-electron mobility transistor. Such spontaneously induced charges at the interface yield normally-on characteristic behavior in a field-effect transistor. Towards an electrical device application, we have recently found that the internal electric field in superlattices causes threshold voltage shift in transistor operations. Here, we introduce a new approach to tune the transistor characteristics of a polar-semiconductor field-effect transistor.

ZnO-related compounds are one type of polar-oxide semiconductors, whose spontaneous polarization are the largest among all Wurtzite crystal structures. At the heterointerfaces of MgZnO/ZnO, high-mobility two-dimensional (2D) electrons are accumulated [1] that exhibit integer and fractional quantum Hall effects [2]. By applying the 2D electrons as a conducting channel in a field-effect transistor (FET) [3], we can obtain normally-on transistor operation for FETs based on ZnO and GaN. Tuning the threshold voltage (V_{th}) is of great importance for reliable operation of the FET.

Although the bilayer structure displayed in Fig. 1(a) is a representative example of polar-semiconductor FETs, the V_{th} of the FET is negative, indicating normally-on operation (orange line in Fig. 1(d)). The tunable parameters being limited to only the Mg-composition and thickness of the structure [2,3], tuning the V_{th} of the bilayer FET is not easy. To address this problem, we have recently examined the performance of superlattice FETs for tuning the V_{th} .

By applying superlattices to the FET, we can expand the number of tunable parameters to include the total thickness of MgZnO and ZnO, thickness ratio, and number of periods in addition to Mg composition. In fact, two types of FETs composed of different superlattice structures, as shown in Fig. 1(b) and (c), exhibit a clear V_{th} shift, shown as red and blue lines, respectively, in Fig. 1(d). The best performance is displayed as a green line in Fig. 1(d), providing a large saturation current with normally-off operation.

The systematic tuning of the V_{th} in FET operation is demonstrated by the insertion of polar-semiconductor superlattices. Although we need further investigation to clarify the dominant parameter in these superlattice FETs, this tuning concept can be widely applied to electrical and optical devices based on polar semiconductors.

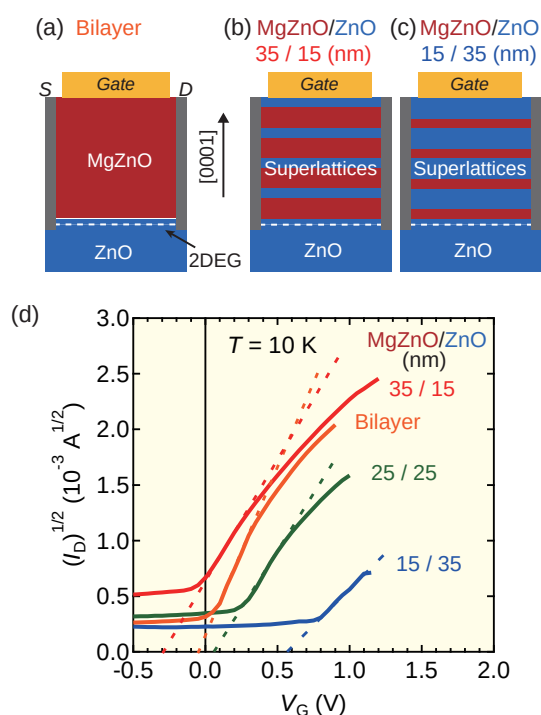


Fig. 1 (a-c) Schematic cross-sectional FET structures composed of a bilayer (a) or superlattices (b and c). S and D indicate source and drain electrodes. White broken lines represent two-dimensional electron gas (2DEG) at the interface. (d) Drain current is presented as a function of gate voltage. Threshold voltage is controlled via internal electric field in the superlattices.

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Keywords: oxide, field-effect transistor, devices

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Charge Fluctuations in Multiorbital Organic Molecules in (TTM-TTP) I_3 with One-Dimensional Structure

Charge fluctuation is a fundamental issue for strongly correlated organic molecular systems. Recent discoveries of charge dynamics in molecular dimers in Mott insulators reveal new aspects of charge degrees of freedom in organic molecular systems. We have detected charge fluctuations and freezing in multiorbital molecules in an one-dimensional organic crystal of (TTM-TTP) I_3 by observing its dielectric properties.

Organic molecular systems have numerous charge degrees of freedom compared with alloys and transition-metal oxides because of the complexities of their molecular shapes and arrangements. Recent observations of charge degrees of freedom in molecular-dimer structures [1, 2] provide possibilities of new functionalities and deep insights into the fundamental understandings of Mott transition. In a Mott insulator, when a charge in a molecular dimer shifts to either molecule, an electrical dipole emerges and its corrective dynamics change the dielectric properties. Even in a molecule with a multiorbital structure, an analogy can be drawn as shifts of charges within different orbitals.

(TTM-TTP) I_3 is a strongly correlated system composed of TTM-TTP molecules. TTM-TTP has two segments on the basis of which the molecular electronic states can be considered. The fragments play a critical role in the charge ordering transition in this system [3]. Therefore, this system is suitable for a study of the charge degrees of freedom within the molecule. Here, we have measured the dielectric properties of (TTM-TTP) I_3 and observed charge fluctuations and freezing in the fragments of the molecules [4].

Figure 1(a) shows a schematic of the molecular arrangement of the (TTM-TTP) I_3 crystal. The arrows indicate the molecular long and short axes. The two fragments are represented by broken lines. The temperature dependence of the dielectric constant is shown in Fig. 1(b). In the direction of the molecular long axis, we can see a large anomaly at around 15–30 K, but it is small along the molecular short axis. These results correspond to the directions of the fragments in the crystal. As the frequency becomes higher, the peak-top temperature increases, as shown by the open circles in Fig. 1(b). This is due to the emergence of a relaxor-like inhomogeneous electronic state. Below 10 K, the anomaly is suppressed and the dielectric constant

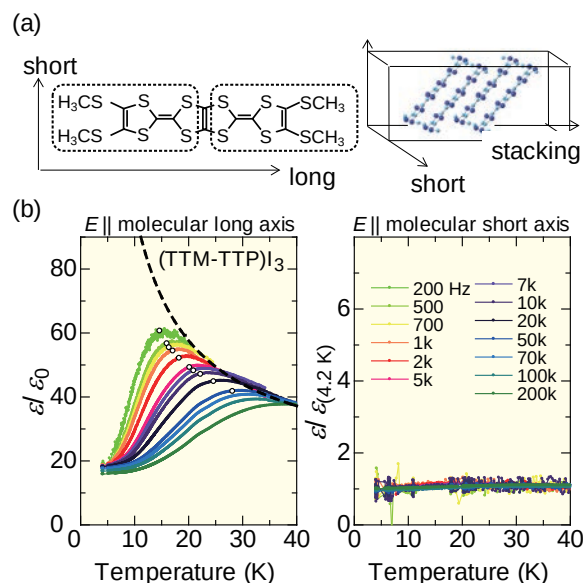


Fig.1 (a) Schematics of (left) TTM-TTP molecular and (right) crystal structure. (b) Temperature dependence of dielectric constant for each direction.

becomes independent of temperature. This indicates the freezing of the glassy dynamics of the charges in the TTM-TTP molecules. Our results confirm that charge dynamics exist in the multiorbital molecular system.

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Combined Study of Neutron and X-ray Inelastic Scattering Measurements on Electron-Doped Copper-Oxide Superconductors

The evolution of electronic (spin and charge) excitations in carrier doping is an extremely important issue in superconducting copper oxides. Here, we combined neutron and X-ray inelastic scattering measurements on electron-doped superconductors and have revealed a highly itinerant character in the spin and charge excitations, that contrasts with the hole-doped superconducting compounds.

High- T_c copper-oxide superconductivity appears with carrier doping in Mott insulators, regardless of the sign of the carrier. Doping evolution of spin and charge correlations is crucially important for understanding the emergence of superconductivity. Neutron and X-ray inelastic scattering measurements have played a major role in this. For hole-doped cuprates, the spin-wave-like magnetic dispersion originating from a local spin character of the undoped parent compound changes with hole doping to the so-called "hourglass" shape at low-energy regions below E_{cross} ; however, the magnetic dispersion above E_{cross} remains almost unchanged with the spin wave. In the representative electron-doped superconductor $R_{2-x}\text{Ce}_x\text{CuO}_4$ ($R = \text{Pr, Nd, Eu, ...}$), the magnetic dispersion changes in a different way from hole doping: the magnetic excitation remains commensurate at low energies. For more information about higher energy magnetic excitation, we exploited complementarily a combination of resonant X-ray scattering (RIXS) and neutron inelastic scattering (INS) to cover high-energy and wide-momentum transfers [1].

From the energy spectra of RIXS at the Cu L_3 -edge, we have observed a dominant single-magnon excitation peak for electron-doped $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. Figure 1(a) shows the magnetic dispersion of the observed single-magnon excitation. The magnetic dispersion of $\text{Pr}_{1.4-x}\text{La}_{0.6}\text{Ce}_x\text{CuO}_4$ (PLCCO) with $x = 0$ observed from INS is also plotted. We find that the magnetic excitation shifts to a higher energy in a wide momentum space upon electron doping. Another additional excitation mode has been observed in the L_3 -edge RIXS spectra at a higher energy than the single-magnon excitation. The peak position of this excitation is plotted in Fig. 1(b) on the background of the color map of the Cu K-edge RIXS for $x = 0.15$. Considering that spin-flip transitions are forbidden in K-edge RIXS, this additional excitation mode in the L_3 -edge RIXS spectra can be assigned to a charge excitation. As deep mixing of the magnetic and charge excitation is observed, we

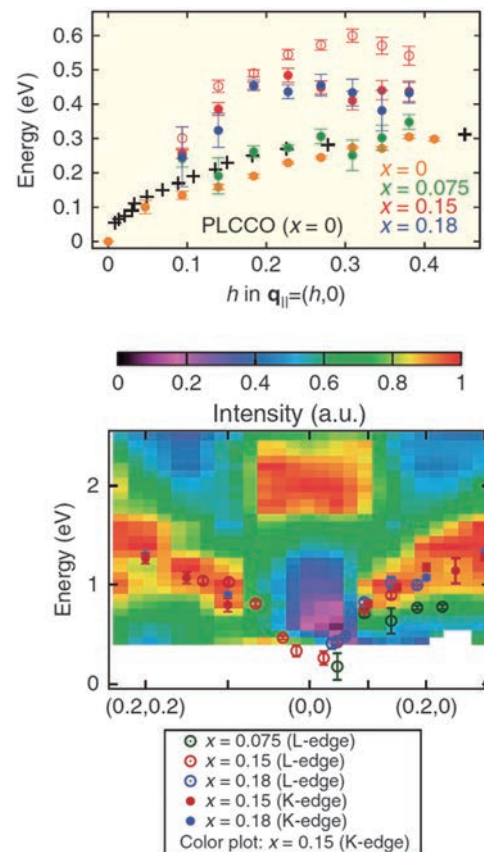


Fig. 1 (a) Peak positions of magnetic excitation for $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (NCCO) observed from RIXS at L_3 -edge and for $\text{Pr}_{1.4}\text{La}_{0.6}\text{CuO}_4$ observed from INS. (b) Peak positions of charge excitation for NCCO and color plot for NCCO with $x = 0.15$ observed from RIXS [1].

conclude that the excitation is dominated by itinerant electron nature. These results are in stark contrast to the hole-doped compounds, where localized spin excitation persists up to high doping levels.

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Atom Probe Analysis of Dopant and Contaminant Diffusion on Silicon Introduced by the Molecular Doping Method

Fabrication of next-generation nanoscale semiconductor devices requires precise placement of dopant atoms into their crystal lattice. Molecular doping combined with a conventional spike annealing method provides a bottoms-up approach that is potentially viable for large-scale production. Here, we highlight atom probe studies of phosphorus doping on silicon.

Ultrashallow doping of Si is one of the key issues of future metal oxide semiconductor microelectronics. Recently, molecular doping has attracted much attention and promises fast doping of entire wafers, and has proven to be effective for the introduction of P (n-type dopant) based on molecular diethyl 1-propylphosphonate, (DPP) at the near surface of semiconductor materials by taking advantage of the self-limiting surface reaction properties of Si. An understanding of the behavior of doped P is essential to confirm the scalability of the method.

Atom probe tomography (APT) enabled us to obtain three-dimensional distributions of individual atoms in semiconductor materials on the order of atomic-scale resolution [1, 2]. Here, we report on the diffusion of P and contaminants such as C and O atoms forming the precursor molecules in the first atomic layers by means of APT [3].

Figure 1(a) shows a series of P doping using DPP and the location of needle specimens for APT analysis. Figure 1(b) and 1(c) show APT maps of samples annealed at 800 and 1025°C, respectively. Interestingly, P diffuses more into Si substrates, although the diffusion coefficients of C and O are larger than that of P in intrinsic Si. While C is directly provided by the decomposition of DPP molecules at the Si interface, O diffuses mostly from the SiO₂ cap layer. However, because of the high reactivity to Si, C and O diffusion appears to be limited to the interfacial region, which extends to 2–3 nm.

Directed self-assembly may be used in large-scale industrial processes provided one includes an additional step to remove the first sacrificial layers in order to eliminate the contaminants.

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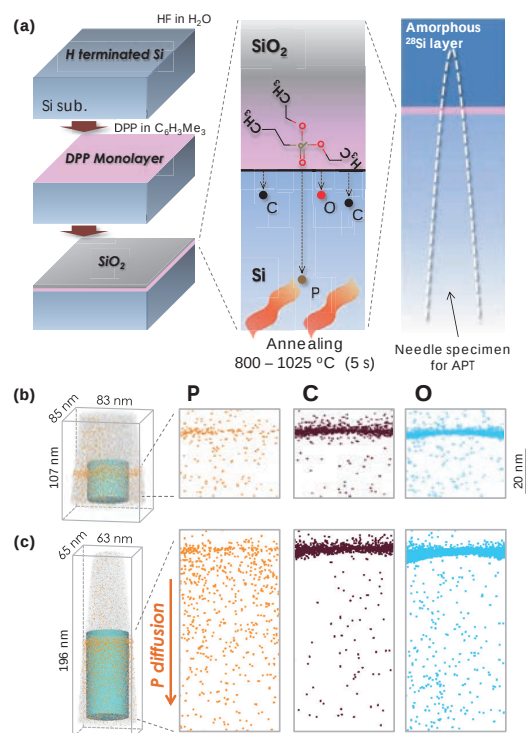


Fig. 1 (a) Sample preparation by molecular doping and position of the needle-shaped specimen for APT. P, C, and O distributions in the samples spike-annealed at (b) 800°C and (c) 1025°C.

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Keywords: atom probe tomography, 3D structure, electronic material

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Electrical Monitoring of Gas Adsorption in Structurally Flexible Porous Coordination Polymers

The gate-opening adsorption behavior of a one-dimensional chain compound was electronically monitored *in situ* by measuring its permittivity and impedance under applied AC electric fields. The gate-opening transition was accurately detected by a sudden change in the real part of permittivity. Furthermore, the imaginary part of permittivity effectively captured the electronic perturbations of the sample induced by the introduced guest molecules. Only the introduction of NO resulted in the increase in the sample's electrical conductivity.

In recent years, porous molecular materials, referred to as porous coordination polymers (PCPs) or metal organic frameworks (MOFs), have attracted much attention as selective gas adsorption materials. Selective gas adsorption is largely achieved by creating host-guest interactions and/or guest-induced gate-opening structural transformations that only occur in the presence of a specific gas molecule [1, 2]. Here, we propose the use of *in situ* AC electric field measurements not only for accurately monitoring such gate-opening gas adsorption of PCPs/MOFs, but also for understanding the electronic effect due to the host-guest interaction [3].

The gate-opening adsorption behavior of the one-dimensional chain compound $[\text{Ru}_2(4\text{-Cl-2-OMePhCO}_2)_4(\text{phz})]$ ($4\text{-Cl-2-OMePhCO}_2^- = 4\text{-chloro-}o\text{-anisate}$; $\text{phz} = \text{phenazine}$) [1] for various gases (He, O_2 , NO, and CO_2) was electronically monitored *in situ* by applying AC electric fields to pelletized samples (~ 5 mg). The gate-opening and -closing transitions induced by gas adsorption/desorption, respectively, were monitored by a sudden change in the real part of permittivity (ϵ' , Fig. 1(a)). Furthermore, the imaginary part of permittivity (ϵ'') effectively captured the electronic perturbations in the samples induced by the introduced guest molecules. The introduction of NO resulted in an increase in the sample's electronic conductivity (σ_{ac} , Fig. 1b), indicating that NO molecules interact with the frameworks through electronic host-guest interactions.

This technique involving the *in situ* application of ac electric fields is useful not only for rapidly monitoring gas sorption responses accompanied by gate-opening/-closing structural transitions, but also potentially for the development of molecular framework materials such as chemically-driven electronic devices.

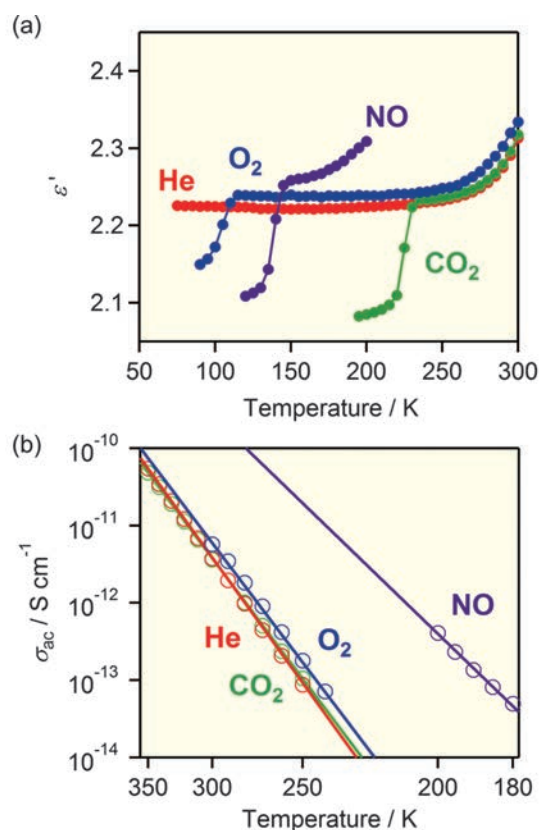


Fig. 1 (a) Temperature dependence of the dielectric permittivity (ϵ') under 100 kPa of various gases. (b) Arrhenius plots of AC electric conductivity (σ_{ac}), which was significantly enhanced under NO atmosphere.

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Nano-Oscillator Using Spin Precession in Half-metallic Heusler Alloys

Spin torque, which originates from the spin angular momentum transfer between local spins and conduction spins, induces spin precession in a nanomagnet. This provides us with a novel spintronic application of a nano-oscillator, called “Spin Torque Oscillator.” We successfully enhanced the output power together with a narrow oscillation linewidth by exploiting a giant magnetoresistance stack with half-metallic Heusler alloys that have high spin-polarization of conduction electrons.

A spin torque oscillator (STO) is an intriguing device based on spin dynamics in a nanomagnet triggered by spin torque. This is a prospective nanometer-scaled radio frequency (RF) oscillator, *e.g.*, for on-chip communications or radar. When a direct electric current (I_{dc}) is applied to a giant magnetoresistance (GMR) device or a magnetic tunnel junction consisting of two ferromagnets separated by a nonmagnetic metal or an insulator, spin torque induces steady spin precession in the ferromagnet; this results in time-dependent device resistance ($R(t)$) through the magnetoresistance (MR) effect. The product of I_{dc} and $R(t)$, therefore, gives the RF voltage (V_{rf}).

Although its simple architecture composed of a single nanometer-scaled element is one of the greatest advantages of the STO, several crucial issues need to be solved before STOs can be put into practical use. One of them is the enhancement of RF output power. We also need to narrow the oscillation linewidth. One promising way to enhance the RF output power is to use ferromagnetic materials showing a large MR effect, *i.e.*, highly spin-polarized materials.

We fabricated current-perpendicular-to-plane (CPP) GMR devices using the half-metallic Heusler alloy of $\text{Co}_2\text{Fe}_{0.4}\text{Mn}_{0.6}\text{Si}$ (CFMS) in order to develop high-power STOs. Figure 1(a) shows an illustration of nanopillar-shaped STO with the CPP-GMR stack of CFMS / Ag / CFMS. When I_{dc} was injected into the CPP-GMR stack, the spin torque excited spin precession in the upper CFMS layer, leading to the V_{rf} output. Because of a large GMR ratio of 30%, we enhanced the output power “to the maximum of 23.7 nW (shown in Fig. 1(b)) with the magnetic field (H) applied normal to the device plane [1]. The micromagnetic simulation suggested that an out-of-plane precession mode was induced. However, non-uniform magnetic structures due to the non-uniform effective magnetic field (H_{eff}) were also observed during the spin precession, which is not suitable for a stable operation of the STO. We also fabricated a point-contact STO having uniform H_{eff} , in which the μm -sized CFMS layer had an nm-sized point

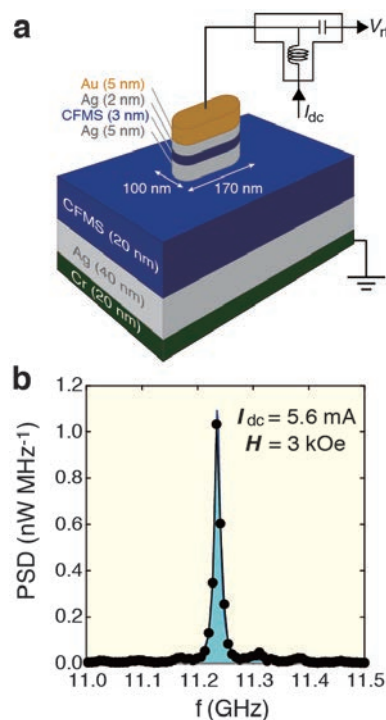


Fig. 1 (a) A schematic illustration of a nanopillar-shaped spin torque oscillator (STO) with the giant magnetoresistance stack of $\text{Co}_2\text{Fe}_{0.4}\text{Mn}_{0.6}\text{Si}$ (CFMS) / Ag / CFMS. (b) An RF spectrum exhibiting a large output power and a narrow oscillation linewidth.

contact region and the I_{dc} flow was confined at the contact. For the point-contact STO, a vortex-like oscillation mode was excited. The uniform H_{eff} enabled us to obtain narrower oscillation linewidth than the nanopillar-shaped STO [2]. We believe that our STOs with CFMS layers have paved the way to realize a high-performance nano-oscillator.

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Keywords: half-metal, spin transfer, spintronics
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Growth of Al-doped $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ Single Crystals for Applications in Piezoelectric Acoustic Devices

Al-doped $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ single crystals with various Al concentrations were grown by the micro-pulling-down method and Czochralski method. The potential of these crystals as a low-power consuming oscillator alternative to a quartz crystal was demonstrated through experiments and calculations using accurate material constants and their temperature coefficients measured by the ultrasonic microspectroscopy technology.

Langasite-type single crystals belonging to point group 32 of the trigonal crystal system with $\text{A}_3\text{BC}_3\text{D}_2\text{O}_{14}$ structure are promising materials for pressure sensors operating in a high temperature environment as well as high stability acoustic devices for future communication applications. In particular, they are potential candidates as alternative materials for α -quartz from the viewpoint of large electromechanical coupling factor, low impedance, and superior temperature stability. In 2000, compounds with ordered structure, such as $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ (CTGS) and $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ (CNGS) were developed because compounds with disordered structure, such as $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS), $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ (LTG), and $\text{La}_3\text{Nb}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ (LNG) cause higher acoustic losses and non-uniform mechanical properties. Although CTGS and CNGS have no rare-earth elements unlike previous langasite-type crystals such as LGS, LTG, and LNG, they still include the expensive element Ga. The substitution of Al for Ga in CTGS and CNGS crystals can dramatically decrease the cost of manufacturing. Besides, there are some reports that Al-substitution provides better piezoelectric properties. Hence, our research group has been engaged in the development of Al-doped CTGS and CNGS single crystals.

We successfully grew highly transparent $\text{Ca}_3\text{Ta}(\text{Ga}_{1-x}\text{Al}_x)_3\text{Si}_2\text{O}_{14}$ crystals with various Al concentrations of $x = 0, 0.2, 0.4, 0.6, 0.8$, and 1 by the micro-pulling-down method (Fig. 1(a)) [1]. Their crystal structures were analyzed by powder X-ray diffractometry resulting in a single phase of the langasite-type structure. Their lattice parameters related to the a- and c-axes systematically decreased with increase in Al concentration. It followed from the EPMA analysis that the actual Al concentration in the crystals almost corresponded to the nominal compositions. From this result, it is confirmed that Al-substituted CTGS single crystal can be grown from a stoichiometric melt.

Based on this result, we attempted to grow $\text{Ca}_3\text{Ta}(\text{Ga}_{0.5}\text{Al}_{0.5})_3\text{Si}_2\text{O}_{14}$ (CTGAS) single crystal with a diameter of 1 in. by the Czochralski method [2]. The

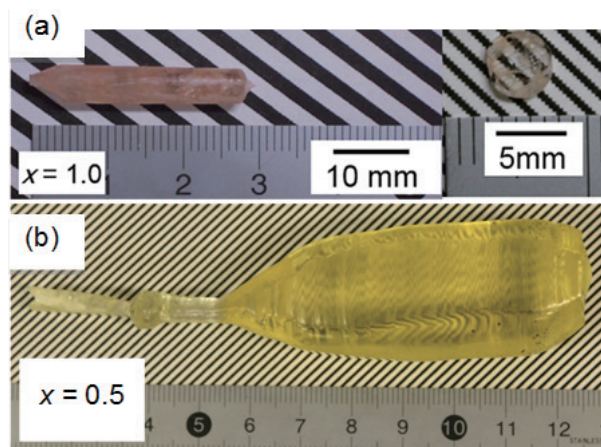


Fig.1 $\text{Ca}_3\text{Ta}(\text{Ga}_{1-x}\text{Al}_x)_3\text{Si}_2\text{O}_{14}$ single crystals grown by the μ -PD method (a) and by Czochralski method (b).

grown crystal was transparent with a yellow color and had no cracks (Fig. 1(b)). Elastic constants, piezoelectric constants and its temperature coefficients were accurately determined from bulk acoustic wave velocities as well as dielectric constants and the density measured for the CTGAS specimens using ultrasonic microspectroscopy (UMS). It was demonstrated that the constants determined could provide calculation accuracy within $\pm 0.15\%$ in the leaky surface acoustic wave (LSAW) velocity. Numerical calculations using the constants determined predicts that there is a cut angle where the temperature coefficient of shear wave velocity becomes zero around 148°Y-cut exhibiting an electromechanical coupling factor of $k^2 = 3.2\%$, which is about four times larger than that of AT-cut quartz. This new crystal will contribute to achieving superior piezoelectric devices for future mobile communications.

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Field Reentrant Superconductivity and Fermi Surface Instabilities in Uranium Ferromagnetic Superconductors

The field reentrant superconductivity of uranium ferromagnets has recently attracted significant interest because an unconventional mechanism of superconductivity is realized. The enhancement of the effective mass and field-induced ferromagnetic fluctuations play key roles for the reentrant superconductivity. In this study, we found that the associated Fermi surface reconstructions, which are often detected as Lifshitz-type transitions, also play a key role through transport measurements under extreme conditions.

The coexistence of ferromagnetism and superconductivity is currently a topic of great interest in condensed matter physics because an unconventional mechanism of superconductivity has been realized. One can naturally consider the triplet spin state with equal-spin pairing in ferromagnetic superconductors because it is robust against the strong internal field caused by ferromagnetism. Moreover, the superconducting upper critical field H_{c2} is not governed by the Pauli paramagnetic effect. Thus, unusual field-induced superconducting phenomena are expected. Figure 1 shows the temperature–field phase diagram of URhGe when the field is applied along the hard magnetization axis. Surprisingly, the superconductivity reappears at high magnetic fields from 10 to 13 T. Because the superconducting transition temperature is rather low ($T_{sc} = 0.25$ K), H_{c2} at 0 K is expected to be less than 1 T. However, the reentrant superconductivity appears at much higher fields. More surprisingly, the maximum temperature (approximately 0.4 K) of the reentrant superconducting dome in Fig. 1 is even higher than T_{sc} at zero field. This confirms that the magnetic field reinforces the superconductivity. The key point is the field-induced ferromagnetic fluctuations. As shown in Fig. 1, the ferromagnetic Curie temperature T_{Curie} is suppressed with increasing field and finally reaches zero with a weak first-order transition. The suppression of T_{Curie} indicates that the ferromagnetic fluctuations are strongly induced by the magnetic field together with the enhancement of the effective mass.

Recently, we more precisely studied the field reentrant superconductivity and ferromagnetic fluctuations by means of measuring the Hall effect, thermopower, and quantum oscillations. Figure 2 shows the field dependence of the Hall resistivity at different temperatures [1]. The Hall resistivity originates from both the normal and anomalous Hall effects. After subtracting the anomalous Hall effect, it is found that the carrier number is significantly changed at the suppression of T_{Curie} , indicating the drastic reconstruction of the Fermi surface. Further

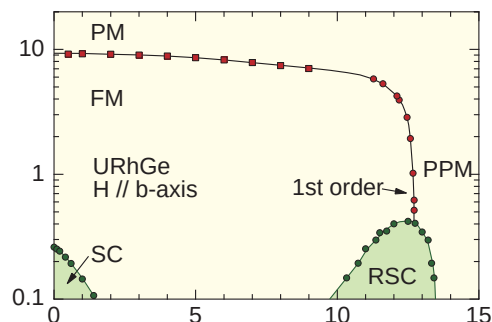


Fig. 1 Temperature-field phase diagram of the ferromagnetic superconductor URhGe for the field along b-axis. The reentrant superconductivity (RSC) appears at high fields. SC, PM, FM PPM denote superconductivity, paramagnetism, ferromagnetism and polarized paramagnetism, respectively.

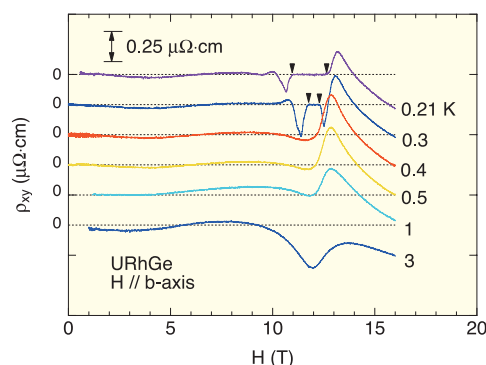


Fig. 2 Field dependence of Hall resistivity in URhGe at different temperatures.

direct evidence was also obtained from quantum oscillation and thermopower measurements. This Fermi surface reconstruction is most likely caused by the Lifshitz-type transition associated with magnetic instabilities related to significant changes in the ferromagnetic sublattice moment.

This work was conducted in collaboration with G. Knebel, A. Pourret, and J. Flouquet in CEA Grenoble.

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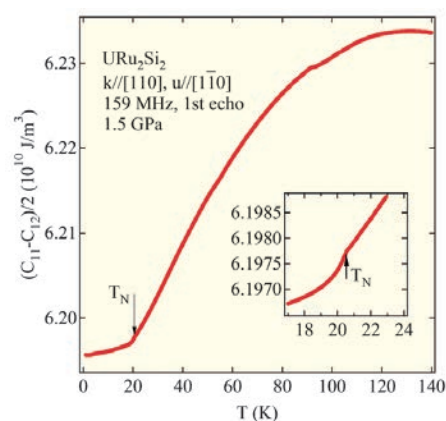


Progresses in Ultrasonic Measurements for Studying Actinide Physics and Development of Hydride Material for Nuclear Reactors

International Research Center for Nuclear Materials Science

In the field of actinide science, an ultrasonic measurement system for studying actinide compounds under pressure has been developed. The elastic constant of URu_2Si_2 has been measured at a pressure of 1.5 GPa. In the field of nuclear materials, a hydride neutron absorption material has been developed. An irradiation test of the hydride in the BOR-60 reactor in Russia has been successful.

Pressure experiments are powerful tools to control the electronic state in actinide compounds. In collaboration with the groups of Prof. Settai and Prof. Nemoto at the Niigata University, we have succeeded in developing a pressure cell up to 3 GPa for conducting electric, magnetic, and elastic experiments for relatively large actinide compounds. Ultrasonic experiments under pressure were limited to about 1 GPa before now, because of the difficulty in sample setting with a transducer and coaxial cable for a high-frequency signal in a small space. Figure 1 shows the temperature dependence of the elastic constant of the $(C_{11}-C_{12})/2$ mode in URu_2Si_2 at (a) ambient pressure and (b) 1.5 GPa. The single crystal of URu_2Si_2 was grown in Prof. Aoki's group at Oarai. URu_2Si_2 is an intriguing compound with a hidden ordered phase at $T_0 = 17.5$ K. With increasing pressure, the antiferromagnetic state appears at 0.5 GPa and the hidden order state disappears from about 1.3 GPa. The elastic constant of the $(C_{11}-C_{12})/2$ mode shows softening below 100 K indicating that the crystalline electric field states relate to the hidden order phase. The peak position moves to a higher temperature at 1.5 GPa. Experiments under pressure and detailed analyses will be performed in



(b) 1.5 GPa

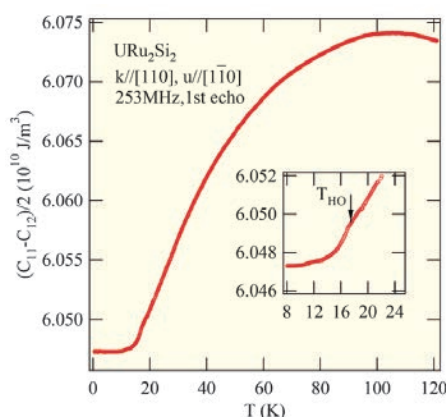
Fig. 1 Temperature dependence of the elastic constant of $(C_{11}-C_{12})/2$ mode in URu_2Si_2 .

the near future to further study the hidden order phase of URu_2Si_2 .

Metal hydrides have a high hydrogen-atom density equivalent to that of liquid water. Hafnium hydride has been investigated as a neutron absorber in Fast Breeder Reactors (FBRs). Fast neutrons are efficiently moderated by hydrogen in Hf hydrides and are absorbed by Hf. Because three isotopes of Hf have large cross sections, the life of a control rod can be increased using Hf hydride. Results of a design study of a core with Hf hydride control rods show that a long-lived hafnium hydride control rod is feasible in a large sodium-cooled FBR. Results of an irradiation test conducted in the fast experimental reactor BOR-60 in Russia have demonstrated the integrity of the capsules during irradiation. Compared with a He-bonded capsule, a Na-bonded capsule has an advantage in terms of the confinement effect of hydrogen [1].

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(a) ambient pressure

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Towards Four-Dimensional Electron Tomography (4D-ET)

Cooperative Research and Development Center for Advanced Materials

We have developed a newly designed straining holder for *in situ* transmission electron microscopy compatible with electron tomography. The holder can deform a specimen under tensile stress with variable strain rates. The maximum tilt angle reaches $\pm 60^\circ$. The new specimen holder, termed as “straining and tomography holder,” will have wide range potential applications in materials science.

Electron tomography (ET) was introduced in materials science in the past decade and has opened a new prospect: the technique can reveal three-dimensional (3D) structural information [1-2]. However, a major roadblock exists to combine the *in situ* experiments with electron tomography, which is expected to reveal real-time 3D structural changes. Towards dynamic 3D (*i.e.*, “4D-ET”) visualization of material microstructures under various straining conditions with a time scale of a few minutes or less, we designed and developed a new specimen holder compatible with tensile tests and high-angle tilting, termed as “straining and tomography (SATO)” holder [3].

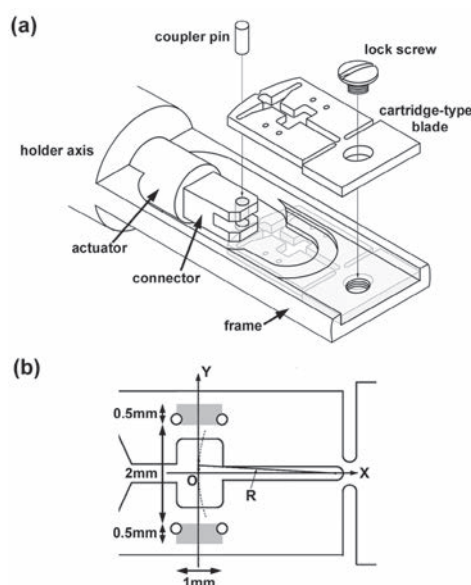


Fig. 1 (a) A schematic illustration of a newly designed specimen holder and (b) a cartridge-type blade on which a specimen is glued. The area of gluing is marked by gray.

The basic concept of this development is a single tilt-axis holder that has a tensile mechanism and is capable of electron tomography. To achieve straining and high-angle tilting simultaneously, we developed a novel mechanism as shown in Fig. 1(a). A linear-motion

actuator deforms a newly designed cartridge-type blade on which a specimen is glued. The deformation velocity of the blade is designed to be 1/3 of that of the actuator. Figure 1(b) explains the motion of blade. The trajectory (dotted line) is an arc, but the radius of curvature (R) is so large (3 mm) that the tensile axis is perpendicular to the holder for a nanometer-scale object whose center is located at O .

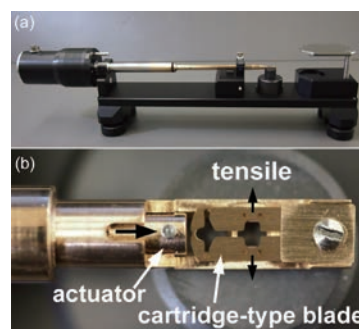


Fig. 2 (a) A developed specimen holder and (b) a magnified photo of a cartridge-type blade.

Figure 2 shows (a) a developed specimen holder and (b) a magnified photo of the cartridge-type blade. The holder motion is fully computer-controlled via a graphical user interface developed for this system.

We measured the deformation velocity of the blade and deduced the strain rate. The minimum and the maximum values obtained were 1.5×10^{-6} and $5.2 \times 10^{-3} \text{ s}^{-1}$, respectively. We confirmed that the blade and the holder are robust and that multiple acquisitions do not raise any technical problem. This result demonstrates the stability and reliability of the holder as a novel *in situ* experimental instrument for 4D-ET.

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Optical Spectroscopy in High Magnetic Fields Using the Hybrid Magnet

High Field Laboratory for Superconducting Materials

High-magnetic-field optical spectroscopy is a very useful method for exploring microscopic states of various condensed matter systems. This kind of measurement, by utilizing an optical fiber and a solenoid-type high-field magnet, has been used since the 1980s; this was recently resumed with the newly installed spectrometer and detection systems at the High Field Laboratory for Superconducting Materials (HFLSM), IMR, Tohoku University. We have developed apparatuses for optical transmission and Raman scattering experiments in very high fields, up to 30 tesla, by using the hybrid magnet.

Optical spectroscopy, which can determine quantum energy levels with high accuracy, has been applied to a wide range of materials. A combination of a high-field magnet and optical spectroscope is a powerful tool to study exotic states induced by high magnetic fields. It also offers unique opportunities to detect intriguing optical phenomena, such as magnetochromism or directional dichroism. We have been able to perform optical spectroscopy measurements in very high fields, up to 30 T, by using the hybrid magnet at the High Field Laboratory for Superconducting Materials (HFLSM), IMR, Tohoku University. The measurement system for optical transmission spectroscopy is shown in Fig. 1(a). Optical fibers are employed to lead light to the sample in the magnet. The system consists of a halogen-tungsten and deuterium lamp as light sources, that cover the spectrum from the near-infrared to the ultraviolet region; a single grating spectrometer; and a thermoelectrically cooled multichannel CCD camera acquire of spectroscopy data with high efficiency. We can also perform Raman scattering experiments in the infrared region, down to 100 cm^{-1} , by using an argon laser as the light source.

Figure 1(b) shows the results of optical transmission spectroscopy measurements of chromium spinel oxide (CdCr_2O_4), which is a typical example of a three-dimensional geometrically frustrated magnet. A field-induced transition to the nontrivial magnetization plateau phase is known to occur at around 29 T in this material in a magnetic field at low temperature. The inset of Figure 1(b) shows the spectrum at zero magnetic field. We assigned the cause of a weak absorption peak at 14115 cm^{-1} to an excitation, and two absorption peaks at 14130 and 14149 cm^{-1} to simultaneous excitations of an excitation and a magnon [1]. By applying magnetic fields, we observed that

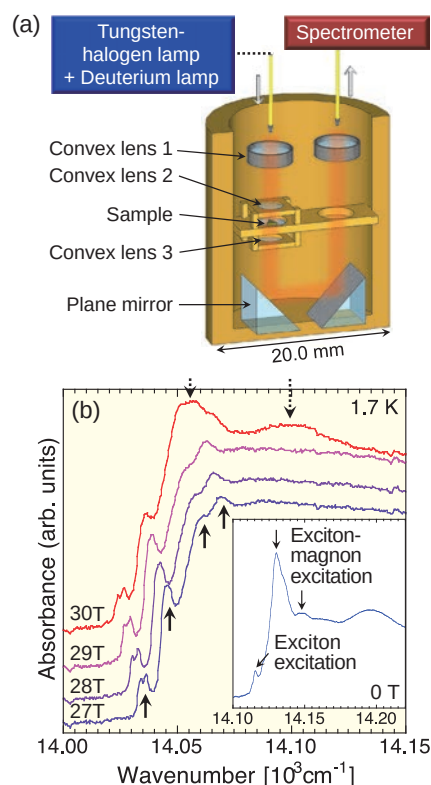


Fig.1 (a) High-field optical transmission spectroscopy system. (b) Field variations of absorption spectra of CdCr_2O_4 .

the exciton peak splits into several peaks, as indicated by the solid arrows. The spectrum is largely changed at 30 T by the transition to the magnetization plateau phase, as indicated by the dashed arrows. The emergence of new peaks at 30 T is attributed to an abrupt change in the density of state of a magnon excitation due to the field-induced transition.

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Scientific Breakthrough towards Creation of New Industrial Materials

Kansai Center for Industrial Materials Research

Institute for Materials Research (IMR) has launched the Kansai Center, a comprehensive institute-wide effort that pairs IMR research groups across the innovation spectrum to solve today's industrial challenges and transform tomorrow's global energy problems. The center was established in April 2011, assuming the responsibilities of the Osaka Center project, based on an agreement between the IMR, the Osaka Prefecture Government, and enterprises in the Kansai area sponsored by the government.

The Kansai Center was established in Osaka as a special unit within the Institute for Materials Research (IMR), Tohoku University, in April 2011 based on an agreement with the Osaka Prefecture Government. The Center is sponsored by the government (Ministry of Education, Culture, Sports, Science and Technology), and it has assumed the responsibilities of the Osaka Center, which carried out its mission from 2006 to 2011. The mission of the Osaka Center was to support small and medium enterprises in the Osaka area. The area covered by the Kansai Center expanded from the Osaka area to the entire Kansai area. The Center has three missions. First, to solve technical problems that industries have struggled to resolve. Solving such problems is occasionally accomplished through collaboration across universities, research institutions, fields, and institutional boundaries. Second, the Center introduces academic research to industries, with the aim of applying them in society. Third, the Center helps educate next-generation materials scientists and researchers in universities and enterprises. To this end, we have organized a bimonthly forum named "Monodukuri Kisokoza," which focuses on special topics regarding materials and processing.

Projects are conducted through widespread collaborations between the government, universities, research institutions, and other organizations. Among them, the Development Center for New Metallic Materials at the Osaka Prefecture University and the Research Center for Nano-Micro Structure Science and Engineering at the University of Hyogo are close partners in collaborative projects, and the Center staff participates in educating students at both universities. The Center has four locations for serving the Kansai area: the Osaka office at Osaka Prefecture University, the Hyogo office at the University of Hyogo, the Sendai office at the IMR, and Monodzukuri Business Information Center Osaka (MOBIO) in the Creation Core Higashi-Osaka, a governmental body where sixteen local universities and one college are located to facilitate collaboration with various industries.

The Center has developed various materials and

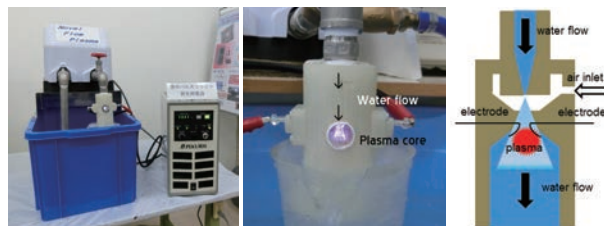


Fig. 1 Prototype device (left), plasma generator (middle), and its schematic structure (right).

processes under collaboration with industry. One of them is to use a plasma system for water purification. Figure 1 shows a prototype device (left) and a plasma generator (middle and right) that generates plasma in water flow and can continuously treat a large amount of water. When water goes through the orifice of the plasma generator, air is spontaneously taken up from the air inlet to provide a cavity of air between the electrodes, which induces breakdown and can maintain plasma in water flow. Because flowing water comes in contact with the plasma core, an enhanced effect can be expected compared to a conventional batch plasma system. In the case of pure water treatment, atmospheric nitrogen molecules entering the plasma were decomposed to form nitrate ions, which is expected to be used as a hydroponic culture nutrient medium. OH radicals and UV generated in the plasma are effective in the sterilization of water or degradation of pollutants in water [1].

Forty similar collaborative studies with industry for practical application utilizing academic knowledge and industrial technology have been in progress. The Kansai Center will make an effort to innovate in the metallic material industry through the alliance with the partners in Kansai area, and promote scientific research in material science.

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Supercomputing for discovery and design of new materials

Center for Computational Materials Science

The Center for Computational Materials Science at IMR supports various advanced studies on computational materials science by providing users with an efficiently tuned high-performance super computer. The total number of users is approximately 150 every fiscal year, producing various fascinating results. Among these, two recent outcomes have been selected and are introduced below. One is by R. Yamada, a graduate student at IMR and the other is by Dr. N. Fujita, a theoretician, at the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University.

First-Principles calculation of Coefficient of Thermal Expansion in Fe-Ni alloys*

First-principles calculation enables us to investigate various physical and thermal properties. The following results were obtained by combining first-principles electronic structure total energy calculations with the Cluster Variation Method.

Fe-Ni alloy is known as Invar, and the temperature dependence of the Coefficient of Thermal Expansion (CTE) at Fe-35at.%Ni shows a non-monotonic temperature dependence. The cause of this abnormal behavior is hypothesized to be the temperature variation in the alignments and magnitudes of magnetic moments [1]. Non-monotonic abnormal behavior, however, was observed even without considering any spin configurations, as shown in Fig. 1. The cause of this temperature dependence in CTE is largely attributed to a change in atomic configurations. This fact gives us new insights into the abnormal behavior of Invar alloys.

Geometrical search algorithm of complex three-dimensional tilings**

As a geometrical framework for describing the cluster packing in icosahedral quasicrystals, 'canonical-cell tiling', or tiling with four types of basic polyhedra as the proto-tiles, has been proposed [2]. In X-ray crystallography, approximant crystals with a chemical composition similar to icosahedral quasicrystals are shown to have crystal structures in which clusters occupy the vertices of a periodic canonical-cell tiling. For representing an icosahedral quasicrystal, a quasiperiodic canonical-cell tiling is indispensable. However, it has never been proved theoretically that the canonical cells can tile the space quasiperiodically. In this study, a computer algorithm for expanding the dimensions of the unit cell of a periodic canonical-cell tiling by a factor of the cube of the golden mean was implemented. An example of

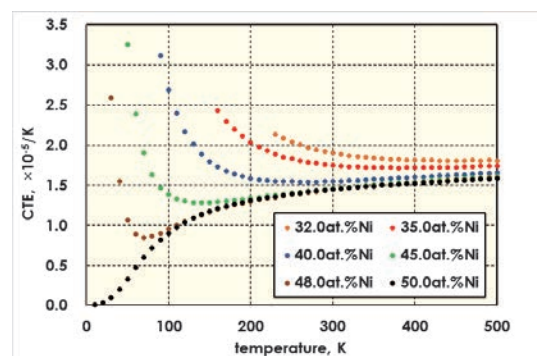


Fig. 1 Coefficient of thermal expansion as a function of temperature.

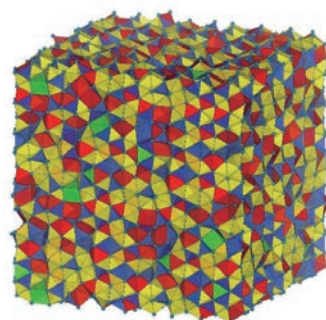


Fig. 2 A new tiling generated by using an original program. This is a complex yet beautiful tiling with space group Pa-3 containing 2464 vertices within the unit cell.

new tilings generated using this program is shown in Fig. 2. This is a complex yet beautiful tiling with space group Pa-3 containing 2464 vertices within the unit cell. A similar approach may lend itself to an attempt to prove the existence of quasiperiodic canonical-cell tiling, that is, a tiling with an infinitely large unit cell.

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Research and Education on Cutting-Edge Energy Materials by Structural and Carrier Control at the Atomic Level

Collaborative Research Center on Energy Materials

In order to attain clean and economical energy systems, new technology is needed to improve efficiency of energy generation and consumption. To that end, it is essential to create technological breakthroughs, such as the discovery of high-performance energy materials that efficiently convert and transport energy.

At the Center, research and development will focus on the creation of advanced energy materials as well as the design of devices that make optimal use of superior material properties. Through joint efforts in science and engineering, we will make inroads into new research frontiers. In addition to promoting top-level research, efforts will be made to expand the human resource potential of young talents trained in trans-disciplinary integrated collaborations.

The following four research divisions are constructed by mixing science- and engineering-field researchers.

- 1) The Spin Energy Materials Division, led by Prof. G.E.W. Bauer, will carry out theoretical and experimental studies on materials, such as ferromagnets, in which the spin degree of freedom significantly affects the charge and energy transport. This division will strive to understand multi-scale physics and materials science in order to develop new material combinations that realize highly effective conversion between heat and electronic currents.
- 2) The Ion Energy Materials Division, led by Prof. H. Miyasaka, will conduct research in both fundamental and applied studies of materials for effective ion transport and chemical energy conversion. The development of novel solid electrolytes and electrode materials toward the realization of high-performance all-solid-state secondary batteries and multi-functional batteries will contribute to building a sustainable society.
- 3) The Light Energy Materials Division, led by Prof. K. Fujiwara, will contribute to the development of a sustainable renewable energy society through the fusion of research on crystal growth physics and electronic engineering.

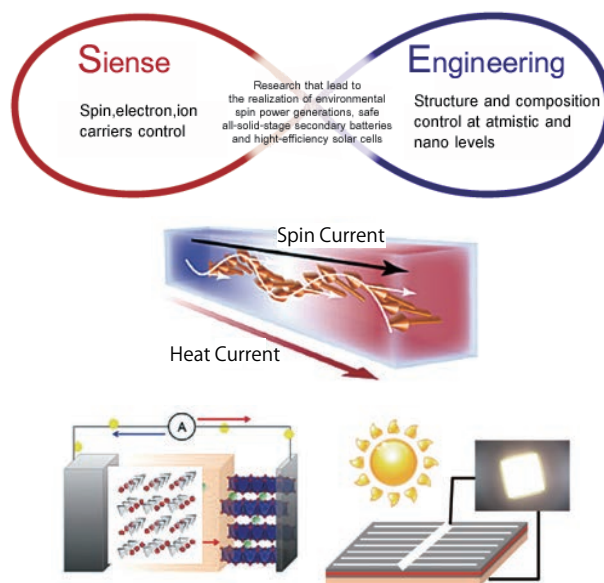


Fig. 1 Realization of environmental spin power generation, advanced all-solid-state secondary batteries, and high-efficiency solar cells, by joint efforts in science and engineering.

- 4) The Material Processing and Social Implementation Research Division, led by Prof. H. Kato, will make research efforts in material processing to produce high-quality and cost-effective energy materials and in developing evaluation techniques to demonstrate performance materials and device abilities. This division will contribute to the construction of a new energy system based on cutting-edge energy materials with the aim of applying the research output of this center to a sustainable society.

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Electrochemical Biocompatibilities of Beta-Type Ti-Nb-Ta-Zr Alloys through Microstructural Refinement

International Collaboration Center (ICC-IMR)

We aimed to investigate the electrochemical behavior of β -type Ti-Nb-Ta-Zr (TNTZ) alloys in this collaboration. *In-vitro* corrosion susceptibilities of the alloys were compared with traditional implant materials such as Ti-6Al-4V and CP Ti in this study. In addition, the effect of high-pressure torsion (HPT) on the corrosion susceptibilities of the alloys was investigated using a simulated body fluid.

Recently, the most common corrosion resistant metallic biomaterials are being made of stainless steel (SS), cobalt–chromium (Co–Cr) alloys, and titanium (Ti) alloys. Ti alloys are frequently used in biomedical applications, particularly because of their higher corrosion resistance, biocompatibility, higher specific strength, and much lower elastic modulus than the other metallic biomaterials [1].

During the visiting period, corrosion susceptibilities of β -type TiNbTaZr (TNTZ) alloys were compared with commercial implant materials such as Ti-6Al-4V and pure Ti (CP Ti). The effect of the high-pressure torsion (HPT) process on the corrosion susceptibilities was also investigated under *in-vitro* conditions at body temperature. HPT is a common technique for the fabrication of Ti alloys with sub-micron grain sizes [2].

Figure 1 shows the potentiodynamic scanning (PDS) curves of the samples in Ringer's solution ($\text{NaCl}=8.60 \text{ g/L}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}=0.33 \text{ g/L}$ and $\text{KCl}=0.30 \text{ g/L}$). The PDS profiles of the samples are quite similar to each other and all samples attain their respective stable passive current densities as the potential increases. In other words, the protective passive films formed on the surfaces were stable. It is well known that protective surface films on the alloys play a key role in the corrosion of metallic implants. However, the passive layers on Ti-6Al-4V alloy are different from that on TNTZ since the oxide layer contains oxides of the alloying elements. The relatively higher corrosion resistance of TNTZ compared to the Ti-6Al-4V alloy is attributed to the formation of Nb_2O_5 , which is chemically more stable, less soluble, and more biocompatible compared to the V_2O_5 formed on the Ti-6Al-4V alloy.

Most investigations showed that the corrosion resistance of an ultrafine, grained alloy is lower than that of its coarse-grained counterpart [3]. TNTZ-HPT shows lower E_{pp} (passivation potential) value and a wider passivation range as compared to the others. This result indicates that the severely strained sample (TNTZ-HPT) is more resistant to corrosion

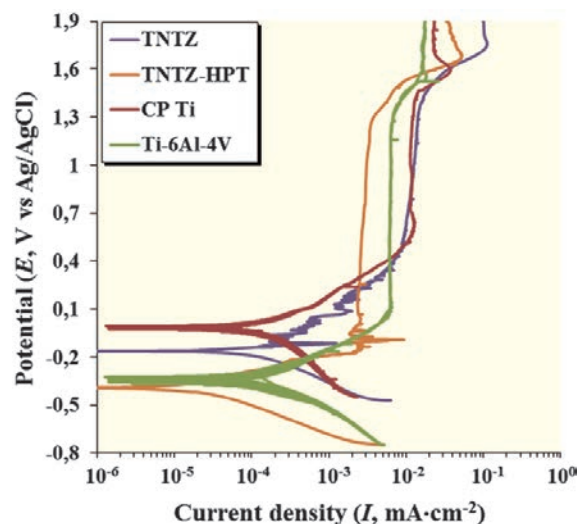


Fig. 1 Potentiodynamic polarization curves of the Ti alloys in Ringer's solution.

than the other Ti counterparts in Ringer's solution. Clearly, there is a strong connection between corrosion resistance and the microstructural features of TNTZ. The supersaturated solid solution decomposes completely and possibly reaches the equilibrium state after the HPT process [4].

I am thankful to the Institute for Materials Research (IMR), especially Professor Niinomi for his valuable contributions to the research. I hope that our future collaboration continues.

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Neutrons for Advanced Materials Science

Center of Neutron Science for Advanced Materials

The Center of Neutron Science for Advanced Materials is a unique neutron facility, which has a background in novel materials science at the IMR. This center operates two neutron spectrometers for materials science investigations in a research reactor facility, and it is constructing a new neutron spectrometer at J-PARC/MLF, which provides the world's brightest neutron beam.

The Center of Neutron Science for Advanced Materials (CN-IMR) was established in 2010 with the aim of promoting novel materials science by using neutrons. The CN-IMR is now constructing a new neutron spectrometer (Fig. 1) at an intense neutron source at the Japan Proton Accelerator Research Complex (J-PARC) [1]. Coupled with state-of-the-art techniques in neutron beam and spin-polarization devices, our spectrometer will provide a unique opportunity to measure microscopic state in materials along with separation of pure magnetic correlations and atomic correlations. The important parts of a spectrometer, such as vacuum chamber and polarization analyzer, were successfully installed in 2014FY, under collaboration with the High Energy Accelerator Research Organization (KEK). We expect to receive the first neutron beam in 2015FY, and the

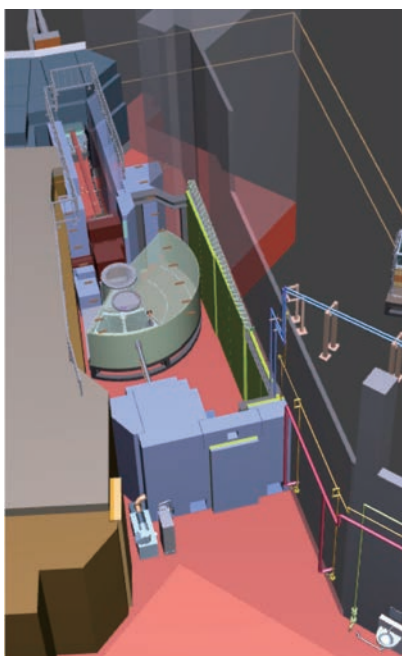


Fig. 1 Illustration of new spectrometer being constructed at J-PARC [1].



Fig. 2 Group photo of participants in the neutron science school organized by CN-IMR.

spectrometer will be available for the collaborative research programs of IMR after commissioning.

Furthermore, the CN-IMR is operating two neutron instruments at the JRR-3 research reactor at the Japan Atomic Energy Agency. Utilizing one of the instruments, a three-day school of neutron science for new users was held from June 2, 2014. Over 20 students and young researchers at Tohoku University attended the program (See Fig. 2) and learned the fundamentals of neutron scattering techniques. Several staff at JAEA, Tokyo University, and J-PARC kindly supported the school by giving lectures and introducing the Materials and Life Science Experimental Facility at J-PARC. The students interacted with senior researchers at the facilities through various discussions. The school received favorable feedback from all the participants, indicating the success of the workshop

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Nanocrystalline Fe-Based Alloys for Commercial Applications

Research and Development Center for Ultra High Efficiency Nano-crystalline Soft Magnetic Material

Nanocrystalline $\text{Fe}_{81.2}\text{Co}_4\text{Si}_{0.5}\text{B}_{9.5}\text{P}_4\text{Cu}_{0.8}$ alloy (at.%) with a low coercivity of 7 A/m and high saturation magnetic flux density of 1.84 T has successfully been reproduced in 50 mm wide ribbons. This suggests that the nanocrystallized Co-containing alloy has high applicability in high-efficiency magnetic core materials.

Modern society is full of a variety of electric products, in which motors, cores, and so forth are used as principal parts. Electricity is an integral part of everyone's life, and thus, we need to use electric power efficiently without wastage under a condition of limited power generation. Use of efficient materials for electric products can decrease the losses. A research strategy in our group is to develop novel Fe-based alloys that contribute to reducing the losses.

Recently, our group has succeeded in developing a novel Fe-based nanocrystalline soft magnetic alloy named "NANOMET®" [1] with high saturation magnetic flux density (B_s), low core loss (W), and low coercivity (H_c). This report includes a study of the NANOMET family alloys for use in products by modifying the alloy components.

Figure 1 shows the outer shape and surface appearance of wide ribbons of 50 mm width, 65 m length, and 25 μm thickness. When using these ribbons in magnetic core applications, W as well as H_c and B_s are of great importance. Figure 2 shows W at 50 Hz as a function of the maximum induction (B_m) of nanocrystalline $\text{Fe}_{81.2}\text{Co}_4\text{Si}_{0.5}\text{B}_{9.5}\text{P}_4\text{Cu}_{0.8}$ (at.%) alloy ribbons where the widths are 10 and 50 mm. Referential data for comparison include the plots of the alloy with commercially-used, non-oriented magnetic steel and Fe-based $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ (at.%) amorphous alloy ribbon (Metglass). This nanocrystalline alloy exhibited W characteristics independent of the ribbon width. The W at a B_m of 1.5 and 1.7 T was determined to be 0.52 and 0.66 W/kg, respectively, for the 50 mm-wide ribbon, and 0.44 and 0.66 W/kg, respectively, for the 10 mm-wide ribbon. These W values are almost the same as those of the ribbon specimens in the laboratory at a scale of several mm. Comparisons of these W data with those of commercial alloys revealed that the present nanocrystalline alloy ribbons showed much lower W at B_m , in particular, above 1.5 T. It is, therefore, concluded that the nanocrystalline $\text{Fe}_{81.2}\text{Co}_4\text{Si}_{0.5}\text{B}_{9.5}\text{P}_4\text{Cu}_{0.8}$ alloy with excellent soft magnetic properties can be fabricated into thick



Fig. 1 Outer appearance of a 50 mm-width ribbon fabricated by melt-spun technology [2].

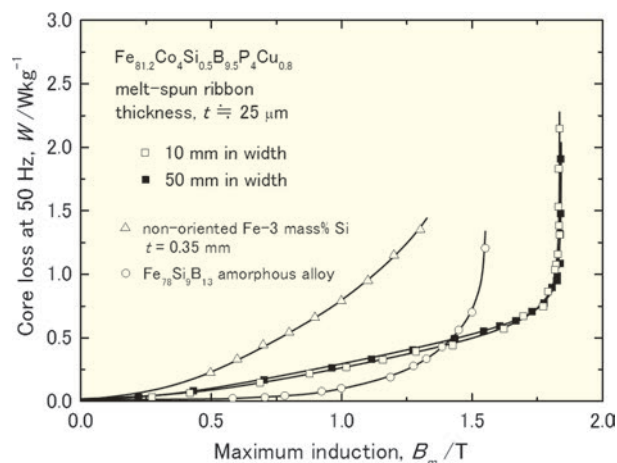


Fig. 2 Core loss at 50 Hz of the nanocrystalline $\text{Fe}_{81.2}\text{Co}_4\text{Si}_{0.5}\text{B}_{9.5}\text{P}_4\text{Cu}_{0.8}$ (at.%) alloy wide ribbon as a function of maximum induction [2]. The data of Fe-3 mass% Si and $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ (at.%) amorphous alloy ribbon are also shown for comparison.

and wide ribbons, which is required for practical use. This makes this alloy a promising candidate for high-efficiency magnetic core materials.

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Visualization of Quantized Vortices in Mesoscopic Superconductors

Laboratory of Low-Temperature Materials Science

The scanning superconducting quantum interference device (SQUID) microscope is a useful tool that visualizes the magnetic field distribution at the sample surface. Using this tool, we succeeded in directly imaging quantized vortices confined in mesoscopic superconductors. In this paper, we highlight the evolution of the vortex pattern with the applied magnetic field in square and triangular superconducting dots.

The physical phenomenon caused by the interaction of a small number of particles in a confinement potential has attracted significant interest. A typical model is a system of quantized vortices in a mesoscopic superconductor, where the vortices are subject to lateral confinement due to the shielding current flowing along the sample edge in addition to the intrinsic repulsive vortex–vortex interaction. The combination of these interactions results in unique vortex states that strongly reflect the sample shape, unlike the well-known Abrikosov triangular lattice in bulk superconductors. To verify this, we employed a scanning superconducting quantum interference device (SQUID) microscope, which visualizes the magnetic field distribution with a high resolution and enables us to directly observe the vortices through their magnetic flux. Here, we demonstrate how the vortex pattern evolves with an applied magnetic field in square [1] and triangular [2] dots of superconducting amorphous $\text{Mo}_{78}\text{Ge}_{22}$ films.

Figure 1 shows typical vortex images for $L = 1$ –16, where L is the number of vortices, in a $76 \times 76 \mu\text{m}^2$ square dot [1]. At $L = 4, 9$, and 16, the vortices form 2×2 , 3×3 , and 4×4 square lattices, respectively, instead of the typical triangular lattices, according to the shape of the superconductor. We experimentally found that for $L \geq 5$, the vortex pattern evolves with a multi-shell configuration based on the following rule. With increasing L up to $L = 9$, the outer shell is first filled while maintaining one inner shell vortex. Increasing L further up to $L = 12$, the inner shell grows while keeping 8 vortices in the outer shell. We also confirm that for $13 \leq L \leq 16$ (not shown), the outer shell grows again while keeping 4 vortices in the inner shell. Thus, the inner and outer shells grow in turn with increasing L , as in Hund's rule, and the corresponding changes occur with the formation of square polygons with multiples of 4 vortices.

In the case of triangular dots, it is found that the

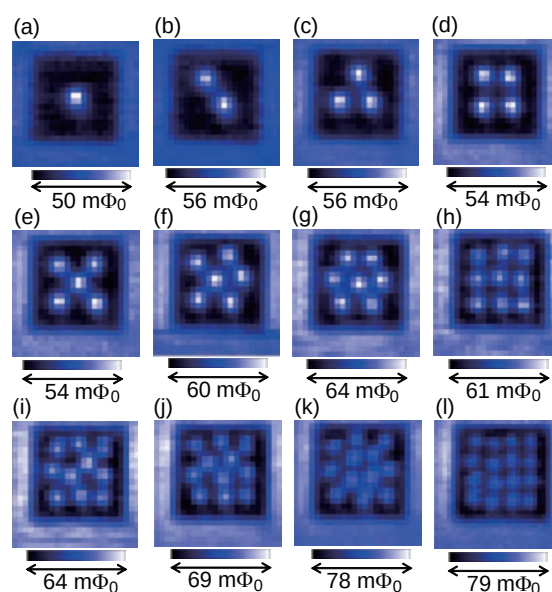


Fig. 1 Typical SQUID images of vortices in the square dot for $L =$ (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 9, (i) 10, (j) 11, (k) 12, and (l) 16 [1]. The color bars indicate the magnitude of magnetic flux per pixel of size $5 \times 5 \mu\text{m}^2$ normalized by the magnetic flux quantum Φ_0 .

field evolution of the vortex pattern occurs in a different way; the vortex configuration can be described as a combination of a triangular pattern and a symmetric linear chain parallel to the base, reflecting the triangular shape of the superconductor [2].

The above insight is obtained by performing repeated observations of vortices in the same samples with continuously increasing magnetic fields. This is made possible by the visualization technique using the scanning SQUID microscope.

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Research Facility for Studying Physics and Chemistry of Radioactive and Nuclear Materials

Laboratory of Alpha-Ray Emitters

More than 170 species of radioisotopes and nuclear materials are available in the Laboratory of Alpha-Ray Emitters. This laboratory is one of the most important centers in the world for studying physical and chemical properties of radioactive materials such as actinide compounds. Researchers, from many leading universities and institutes all over the country, have visited this facility every year to prepare a variety of materials and carry out their chemical and physical measurements.

The laboratory has provided a research environment using 170 radionuclides (RI) and nuclear elements, specifically exemplified by alpha-ray emitters such as actinides. The laboratory started operation in 1960 on the basement floor of the old Main Building 1 of IMR, which was succeeded by the present building in 1978. The laboratory's capacity of RI, including actinide elements, is ranked as the one of the largest among Japanese universities. Recently, this lab has functioned as an important base for preparation of pure crystals of actinide compounds to be provided to other universities and to Synchrotron Orbital Radiation facilities (SORs).

The controlled area of the laboratory consists of three chemistry lab rooms, three physical lab rooms, a room for radioactivity measurements, a contamination test room, and storage rooms for RIs and nuclear materials. Each chemistry lab is equipped with local exhaust ventilation systems. Gamma-ray spectrometers, a liquid scintillation counter, and an alpha-ray spectrometer are installed in the radioactivity measurement room.

Point-contact spectroscopy (PCS) is a method of obtaining differential conductance as a function of a bias voltage ($dI/dV(V)$). The bias voltage V accelerates a passing electron through a point-contact and provides an excess energy eV , which results in the energy spectrum $dI/dV(V)$. When the current I depends on the electrical density of states (DOS) of the system, the $dI/dV(V)$ measurement is suitable for studying the evolution of DOS, such as superconducting gap structure, Kondo resonance peak, etc. Our simple PCS method dramatically widens the measurement conditions to include ultra-low temperature, high magnetic fields, and high pressures. The PCS was applied to actinide compounds with strongly correlated f -electrons, single crystals of which were prepared by the tetra-arc furnace in this lab.

Figure 1 shows the PCS spectra of URu_2Si_2 under two pressures [1]. At 4.2 K, both spectra, under $P = 0.41$ and 0.98 GPa, show a similar structure, with kinks and swells, compared to those at 20 K. Under the

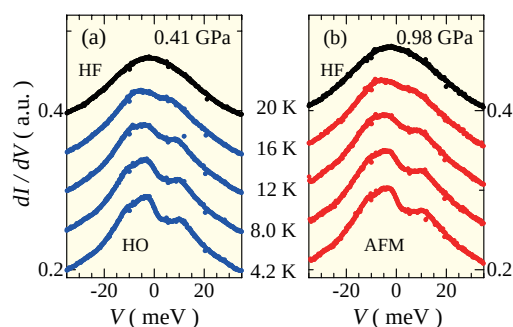


Fig.1 PCS spectra of URu_2Si_2 at (a) HO state at $P = 0.41$ GPa compared with (b) AFM state at $P = 0.98$ GPa.

pressures of 0.41 and 0.98 GPa, URu_2Si_2 exhibits the so-called hidden ordered (HO) state, *i.e.*, the ordered state with an unknown order parameter, and antiferromagnetic (AFM) ordered states at 4.2 K, respectively. At 20 K, URu_2Si_2 shows heavy fermion (HF) behavior under both pressures. The energy dependences of the DOS of HO and AFM are very similar at all temperatures examined. Our results have provided a new relationship between the DOS of the HO and AFM states.

A high-resolution Compton profile (HRCP) measurement, which provides the electron occupation number density (EOND) in k -space, was carried out in the Spring-8 BL08W to visualize the electronic structure in the first Brillouin zone (BZ). We observed that the 2D EOND of $\text{Ce-Ru}_2\text{Si}_2$ significantly changed around the corner of the projected BZ from room temperature to 5 K [2]. We continue to apply PCS and HRCP measurements for investigations on other actinide compounds, such as URu_2Si_2 [3].

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Direct Imaging of Atomic Columns by Using Electron Microscope

Analytical Research Core for Advanced Materials

Quantitative compositional analysis provides useful information in materials sciences. This section supports research activities of IMR by managing and servicing such analytical facilities and techniques. Furthermore, we are also conducting microstructural and crystallographic analyses of materials by using electron microscope for more-reliable research and analysis. Recent observation of NiMnSb and Ni₂MnSb alloys by using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) in an atomic scale is shown here.

NiMnSb alloy is a typical half-metal having a half-Heusler (*C1_b*) structure. Figure 1(a) shows a model of a bcc-based ordered structure that has dimensions of 2 × 2 × 2, including 4-fcc-type sublattices: A, B, C, and D. The A, B, and D sites are occupied by Ni, Mn, and Sb, respectively, with the C sites being vacant in NiMnSb. In the case of full-Heusler (*L2₁*)-type Ni₂MnSb, which is known as a ferromagnetic shape memory alloy, the C sites are occupied by Ni.

Although *L2₁* and *C1_b* structures belong to different space groups—*Fm-3m* and *F-43m*, respectively—both structures have the same extinction rules. Therefore, it is hard to distinguish between these structures by using diffractometry. Thus, the HAADF-STEM method using a JEM-ARM200F is employed here to determine the ordered structures accurately.

The HAADF-STEM images taken from *L2₁*-Ni₂MnSb and *C1_b*-NiMnSb specimens are shown in Fig. 1(b) and (c), respectively. In order to identify the four atomic sites occupied by Ni, Mn, Sb, or vacancy, as shown in Fig. 1(a), the [1-10]_{bcc} axis was chosen as the incident beam direction. All the atomic columns were successfully observed as white dots. Here, the intensity of the atomic column in the HAADF-STEM image is almost proportional to the square of the average atomic number *Z* in each atomic column. The order of brightness for the atomic columns in the present case is Sb > Ni > Mn, as labeled in Fig. 1(b) and (c). In the *C1_b*-NiMnSb alloy, the vacant C sites clearly show a dark contrast, while the C sites in the *L2₁*-Ni₂MnSb alloy show an almost equivalent atomic contrast as that of the Ni A sites.

Furthermore, each atomic contrast pattern observed in these experiments is in almost perfect agreement with that predicted by the simulations as

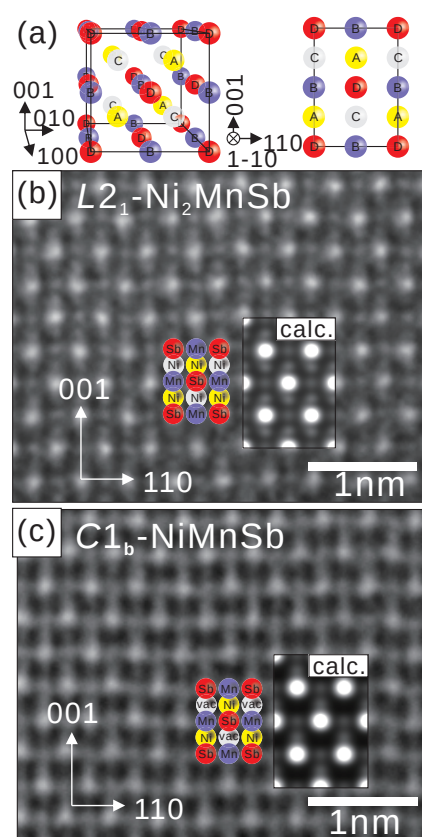


Fig. 1 (a) A schematic of the bcc-based crystal structure. (b) and (c) HAADF-STEM images of Ni₂MnSb and NiMnSb, respectively.

shown in the insets of Fig. 1(b) and (c). Thus, the existence of the vacant site can be satisfactorily confirmed using the HAADF-STEM technique for the first time [1].

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