



Institute for Materials Research, Tohoku University



# KINKEN Research Highlights 2025



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## **KINKEN Research Highlights 2025**

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**G** : GIMRT (Global Institute for Materials Research Tohoku) is a program in which researchers from inside and outside the institute conduct joint research based on a common research theme.

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## Preface

Dear Colleagues,

We are delighted to present "KINKEN Research Highlights 2025," our annual report that showcases research findings from the Institute for Materials Research (IMR) at Tohoku University for the past year. KINKEN is the abbreviation for "Kinzoku Zairyo Kenkyusho," the Japanese name for IMR, and is well known in the materials science community.

IMR has a rich history spanning over one hundred years since its establishment in 1916. Initially, the focus was on iron and steel materials, but as times changed and research progressed, its scope expanded to include the fundamentals and applications of various materials, including non-metals such as semiconductors and ceramics. With these changes, the institute changed its name from the Research Institute for Iron, Steel and Other Metals (RIISOM) to the current one in 1987. Ever since Dr. Kotaro Honda, its first director, invented the world's first artificial permanent magnet called KS magnet steel, the institute has developed many new materials for practical use, including Sendust alloy, SiC fibers, and soft magnetic amorphous alloys, and has also conducted not only fundamental research, but also pioneering research in the search for new materials and the elucidation of physical properties such as magnetism and superconductivity. It has become a global center in materials science.

A key feature of IMR is its integration of fundamental and applied research, as well as science and engineering fields. Additionally, the institute stands out for its joint research with both domestic and international researchers, utilizing world-class facilities for experiments (high-energy irradiation testing, high magnetic fields, supercomputers, etc.) and for the creation and evaluation of new materials. In



Takahiko Sasaki

Director Prof. Takahiko Sasaki

2018, IMR was certified as the International Joint Usage/Research Center for Materials Science, known as "Global Institute for Materials Research Tohoku" (GIMRT). IMR is committed to further promoting research and fostering the next generation of researchers, and putting into practice Dr. Honda's words, "Industry is the training ground of academics," it also focuses on the likes of industry-academia collaboration and engineer training.

IMR is committed to creating a sustainable society, a goal shared by the global community. Its materials science research has the power not only to solve issues but also to positively transform society. The institute is dedicated to supporting the international competitiveness of Japan's materials manufacturing and engaging in global endeavors to create academic intellectual property shared by humankind. IMR will continue to work on innovative materials science research that will bring about a paradigm shift with a long-term vision and contribute to developing human resources who will lead the future.

We hope KINKEN Research Highlights will provide insights into our recent research activities and help encourage worldwide collaboration with IMR. We value your continued support and welcome any suggestions.

## Infrastructural Materials

IMR KINKEN Research Highlights 2025



## Improving Prior Austenite Grain Boundary Coherency Based on Variant Selection in Martensitic Steel

Prior austenite grain boundary (PAGB) is the most vulnerable site for crack propagation in martensitic steel under extreme applications such hydrogen environment and low temperature due to its low coherency. In this study, a strategy to enhance coherency of PAGB was suggested by understanding the relation between austenite misorientation and martensite misorientation at PAGB.

Prior austenite grain boundaries (PAGBs) generally exhibit low coherency. A single austenite grain can transform into 24 different martensite variants based on the Kurdjumov-Sachs orientation relationship (KS OR, (111)FCC// (011)BCC, [-101] FCC// [-1-11]BCC), resulting in 576 (24×24) different orientation relationships at PAGB. Consequently, PAGBs are not homogeneous grain boundaries but are composed of several martensite segments with different OR. While low coherency PAGBs are typically observed, high coherency PAGBs can occasionally form. In such cases, cracks do not propagate. In this study, we investigate the conditions under which this case occurs by analyzing the relation between austenite misorientation ( $\theta_{\gamma}$ ) and martensite misorientation ( $\theta \alpha'$ ) at PAGB [1].

Fe-0.35C-1.0Cr-0.8Mn-0.2Mo-0.3Si steel was used. The specimen was austenitized at 900 °C for 15 min and water quenched. Then, it was tempered at 400 °C for 30 min. The final microstructure was fully martensitic.  $\theta_{\alpha'}$  and  $\theta_{\gamma}$  were measured across PAGBs with and without cracking using electron backscattering diffraction.

Figure 1 illustrates the relationship between  $\theta_{\gamma}$  and PAGB coherency in (a) total and (b) fractured PAGBs. PAGB coherency was evaluated based on the occupancy fraction of low-misorientation ( $\theta_{\alpha'}<10^{\circ}$ ) martensite segments. It was confirmed that PAGB cracking is suppressed when the PAGB coherency exceeds 0.3. To achieve a PAGB coherency greater than 0.3,  $\theta_{\gamma}$  must be either less than 10° or greater than 45°. This is associated with the double KS OR, where the martensite variants formed at the PAGB satisfy the KS OR not only with the parent austenite grain but also with the neighboring austenite grain (double KS OR). This is a prerequisite condition for achieving high PAGB coherency.

For PAGBs with  $\theta_{\gamma}$  less than 10°, the double KS OR is always satisfied, thereby achieving high coherency. Conversely, for PAGBs with  $\theta_{\gamma}$  greater than 45°, only the initially nucleated PAGBs exhibit high coherency. This is attributed to the preferential martensite variant selection that satisfies the double



Fig. 1 Relation between  $\theta\gamma$  and (a) total and (b) fractured PAGBs [1].



Fig. 2 (a) PAGB coherency comparison between martensite and partial bainite specimens (b) PAGB decorated with partial bainite which exhibiting high coherency [2].

KS OR in the initial nucleation stage, minimizing interfacial energy.

Considering that the double KS OR is crucial for achieving high PAGB coherency, decorating PAGB with partial bainitic ferrite was proposed as a method to enhance coherency [2]. This is because bainite is more likely to satisfy the double KS OR due to its lower driving force, which favors interfacial energy minimization. Figure 2 demonstrates that PAGB coherency can be significantly improved, particularly when  $\theta_{\rm Y}$  exceeds 45°. This improvement is attributed to the presence of bainite at the PAGB, which is more likely to satisfy the double KS OR.

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## Large-Scale Molecular Dynamics Simulation for the Design of High Functional Materials and Super-Precise System

o develop highly functional materials and super-precise system, a comprehensive understanding of multiphysics phenomena, including chemical reactions, friction, stress, and fluid dynamics, is essential. We used reactive molecular dynamics simulations and neural network molecular dynamics simulations to investigate these phenomena, with the goal of advancing materials and system design.

The development of highly functional and durable materials is essential in many fields. Achieving this requires a deep understanding of multi-physics phenomena, including chemical reactions, friction, stress, and fluid dynamics. Advances in high-performance computing now make it possible to simulate these phenomena at the atomic scale. Accordingly, we have used reactive molecular dynamics simulations and neural network molecular dynamics simulations to open the way for next-generation materials design [1,2].

Adhesive wear of steel is crucial issue in many industrial fields because it can lead to serious machine failure. However, detailed adhesive wear mechanism is still in debate due to its complexity. This study used reactive molecular dynamics simulations to explore atomic-scale adhesive wear in body-centered cubic iron, focusing on surface orientation, sliding direction, and humidity for improvement of wear resistance of steel. Two wear types were identified: one involves surface deformation, causing severe seizure and the other involves surface fracture, leading to formation of wear debris (Fig. 1). We proposed that the critical conditions determining the adhesive wear type are the rubbing surface orientation and sliding direction. Humid conditions suppressed both wear types, as water-induced chemical reactions formed protective layers on surfaces. Therefore, we concluded that the surface orientation and sliding direction determine the atomic-scale adhesive wear type. whereas humid atmosphere affects the wear amount in atomic-scale [1].

Silicon nitride (Si<sub>3</sub>N<sub>4</sub>) exhibits low friction in aqueous environments due to a tribolayer formed by tribochemical reactions. However, under high contact pressure, where surface contact dominates, this low-friction state fails, showing limited load capacity. Recent experimental studies indicate ethylene glycol (EG) additives improve the load capacity in water, though the mechanism is unclear. This study used neural network molecular dynamics for friction simulations, combining large-scale



Fig. 1 Snapshots of two wear types. (a) Adhesive wear involves surface deformation and (b) adhesive wear involves surface fracture.



Fig. 2 Tribochemical reactions of EG at the sliding interface of Si<sub>3</sub>N<sub>4</sub> produce compounds which consist of carbon, nitrogen, and hydrogen atoms on the Si<sub>3</sub>N<sub>4</sub> surface. [2] http://creativecommons.org/licenses/by/4.0/.

analysis with ab initio accuracy. Results revealed that tribochemical reactions with water generate SiO<sub>2</sub> particles, while reactions with EG produce carbon-, nitrogen-, and hydrogen-based compounds that coat the Si<sub>3</sub>N<sub>4</sub> surface (Fig. 2). We propose that these compounds form a protective layer, enhancing the load-carrying capacity of Si<sub>3</sub>N<sub>4</sub> [2].

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## Intergranular Corrosion of Fe–0.01 wt.% P Alloy: Roles of Grain Boundary Segregation and Misorientation

Grain boundary segregation in Fe-P alloys was analyzed and the effects of the segregated phosphorus and carbon concentrations on intergranular corrosion were assessed. The susceptibility to intergranular corrosion increased with increasing phosphorus concentration at grain boundaries by both heat treatment temperature and grain boundary misorientation. In addition, the intergranular corrosion induced by phosphorus segregation at grain boundaries can be inhibited by carbon segregation.

Grain boundary in metallic materials is known to be segregation site and/or diffusion path of alloying elements and impurities [1-3]. Grain boundaries with segregation of the alloying elements and impurities tend to be preferential sites of material degradation. In this study, we prepared ultralow carbon Fe–P alloy with different heat treatment temperatures and conducted corrosion tests [4]. The grain boundary segregation and misorientation were analyzed using a three-dimensional atom probe and electron backscatter diffraction measurements. Based on the results, the effects of grain boundary segregation and misorientation on intergranular corrosion in Fe–P alloy were discussed.

By comparing the specimens annealed at 600°C and 700°C, the specimen annealed at 600°C had a higher concentration of phosphorus segregation at grain boundaries than that annealed at 700°C. Corrosion was found to occur only on the specimen annealed at 600°C. Figure 1 shows the optical image of the specimen annealed at 600°C taken after corrosion product removal and the corresponding grain boundary map. The corrosion grooves were consistent with the location of the grain boundaries, indicating that the intergranular corrosion occurred on the specimen annealed at 600°C. This result suggests that intergranular corrosion resistance deteriorated with a higher concentration of phosphorous segregated at grain boundaries. Figure 2 shows the number fraction of corroded grain boundaries to total grain boundaries as a function of grain boundary misorientation. The progression of intergranular corrosion increased with grain boundary misorientation up to 30° and became constant at higher grain boundary misorientation. The grain boundary misorientation dependence of corrosion behavior corresponded to the variation in phosphorus concentration at grain boundaries [3]. That is the grain boundary misorientation and associated phosphorus segregation behavior act as factors controlling the intergranular corrosion susceptibility.

Carbon segregation was confirmed only in the specimen annealed at 500°C, and no intergranular corrosion was observed in the specimen despite the highest concentration of phosphorus at the grain



Fig. 1 Optical image of the specimen annealed at 600°C after corrosion product removal and the corresponding grain boundary map.



Fig. 2 Number fraction of corroded grain boundaries to the total grain boundaries as a function of grain boundary misorientation for the specimen annealed at 600°C.

boundary. The intergranular corrosion induced by the high concentration of phosphorous segregation at grain boundaries can be inhibited by carbon, which is identified as an impurity in the alloy. This study paves the way for preventing the macroscopic intergranular corrosion of iron alloys by controlling the elemental segregation of impurities in GBs.

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#### International Co-Authored Paper

## **Multi-Material 3D Printing for Automotive Components**

o address global sustainability challenges such as achieving carbon neutrality and resource conservation, the concept of "multi-materials," which strategically combines different materials for optimal component performance, has become increasingly important. Here, we established the fundamentals for the fabrication of multi-material automotive components using metal 3D printing technologies.

Metal 3D printing technologies create threedimensional objects through layer-by-layer metal deposition, revolutionizing industries and facilitating scientific research. While their primary advantage lies in ability to produce complex, optimized geometries, the technology also enables novel material development through microstructural control during extreme thermal history—a capability increasingly vital for developing high-performance materials [1].

While 3D printing technologies offer unprecedented process flexibility for fabricating multimaterial components, significant challenges persist in practical implementation. A critical limitation arises when joining dissimilar metals commonly used in automotive applications, namely steels and aluminum alloys. The formation of brittle intermetallic compounds at material interfaces substantially compromises structural integrity and has been a longstanding challenge in multi-material manufacturing.

In this study, we employed laser powder bed fusion (L-PBF), a primary metal 3D printing technology, to explore the processability of steel/ aluminum alloy multi-material components [2]. This process uses laser beam to selectively melt metal powder layers according to a 3D computer model. We first optimized building parameters for each material using machine learning algorithms, then investigated the effect of scan speed (550-650 m/s) on interfacial microstructures while maintaining other parameters constant. Our findings reveal that scan speed significantly affects the microstructural evolution at bonding interfaces. This indicates that higher scan speeds promote non-equilibrium solidification through solute trapping, suppressing solute partitioning at the solid-liquid interface during solidification. Consequently, the formation of thermodynamically stable phases, such as Al<sub>5</sub>Fe<sub>2</sub> and Al13Fe4 (typically observed at lower scan speeds) was significantly inhibited (Fig. 1). We validated the in-situ alloying mechanism using numerical simulations.

The optimized process parameters resulted in enhanced bonding strength, as confirmed by tensile

 

 Al alloy (Al3Si1Mn)
 550 mm/s
 600 mm/s
 650 mm/s

 Carbon steel (S25C)
 Image: Carbon steel (Carbon steel (Carbon steel)
 Image: Carbon steel (Carbon steel)

Fig. 1 Effect of scan speed on the interfacial microstructures.



Fig. 2 Bonding strength as measured by tensile testing along the building direction.

#### testing (Fig. 2).

This breakthrough demonstrates the potential of controlled non-equilibrium processing in L-PBF for producing high-performance multi-material automotive components, representing a significant step toward sustainable manufacturing technologies.

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#### International Co-Authored Paper

## Quantitative Analysis of Grain-Boundary Segregation Behaviors of Ca and Y in Magnesium Aluminate Spinel

Grain-boundary structures and chemistry can be significantly influenced by dopant segregation, which may affect to various materials properties such as mechanical and optical properties. In this study, earth-abundant Ca and Y elements were doped in polycrystalline magnesium-aluminate spinel material, and segregation behaviors of those dopants in grain boundaries were quantitatively investigated by various advanced microscopy techniques including quantitative electron backscattering diffraction (EBSD) analysis, atomic resolution imaging and electron energy-loss spectrometry (EELS) analysis.

Magnesium aluminate spinel (MAS, MgAl<sub>2</sub>O<sub>4</sub>) is a unique ceramic material that is transparent over a wide range from UV to mid-IR and presents enhanced toughness, which could be utilized for windows in extreme environments. However, fracture failures tend to occur at grain boundaries (GBs), which is one of the major limiting factors for practical MAS applications. Mechanical properties at GBs can be improved by doping certain elements through modifying atomic arrangements at GBs in MAS. In this study, earth-abundant Ca and Y were doped to polycrystalline MAS to improve mechanical properties.

Grain distributions of undoped, Ca- and Y-doped polycrystalline MAS were characterized by EBSD analysis. Then, grain-boundary characterization distributions (GBCDs) were extracted from the EBSD results. Figure 1 summarized GBCDs for  $\Sigma$ 3 twin boundaries in undoped, Ca-doped, and Y-doped MAS. The positions of the pure twist GB type and the tilt boundaries are indicated by a triangle and a white dashed line, respectively. The undoped spinel sample represents a large anisotropy on the GBCD: higher frequency of twist boundaries than tilt boundaries. After Ca and Y doping, the frequency of tilt boundaries increases, although that of the dominant twist boundaries is reduced. This enhancement of tilt boundaries after doping can be due to modification of GB structures from tighter twist boundaries to more open tilt boundaries in order to accommodate larger Ca and Y dopants [1, 2].

Microstructure and chemistry in the vicinity of the  $\Sigma3$ boundary of the Y-doped MAS were examined by aberration-corrected scanning transmission electron (STEM) with electron energy-loss microscopy spectrometry (EELS) analysis. Figure 2 shows an atomic resolution high-angle annular dark-field (HAADF) STEM image [2]. The brighter regions indicate heavy atomicnumber Y atoms in this imaging mode. So that, the doped Y atoms are segregated at the  $\Sigma$ 3 boundary. Figure 3 shows a Y composition map quantified by EELS analysis in aberration-corrected STEM with a simultaneously acquired HAADF-STEM image, which confirms the Y segregation along the  $\Sigma$ 3 boundary [3].



Fig. 1 Grain-boundary character distributions (GBCDs) of undoped, Ca- and Y- doped MAS, extracted from the EBSD results. The positions of the pure twist grain boundary type and the tilt boundaries are indicated by a triangle and a white dashed line, respectively.



Fig. 2 An atomic-resolution HAADF-STEM image of a  $\Sigma$ 3 twin boundary in the Y-doped MAS. Y atoms are segregated along the  $\Sigma$ 3 boundary.



Fig. 3 A Y composition map acquired in the vicinity of the  $\Sigma$ 3 boundary with a simultaneously acquired HAADF-STEM image, confirming Y segregation along the  $\Sigma$ 3 boundary.

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## Local Hydrogen Entry into Fe Sheets Under Atmospheric Corrosion: Roles of Potential, pH and Rust Layer Formation

Local hydrogen entry under a NaCl droplet on Fe sheets was visualized by using a hydrogenochromic sensor. Hydrogen entry was accelerated under an island-like rust layer because of acidification, and it was prominent under the region covered with a thick rust layer after the disappearance of the droplet, owing to the high concentrations of chloride ions and protons.

Clarifying hydrogen entry behavior into steels owing to corrosion in atmospheric environments is important to overcome hydrogen embrittlement of structural steels. To understand the local hydrogen entry behavior under an atmospheric corrosion environment, we utilized a hydrogenochromic sensor [1-3] consisting of a polyaniline (PANI) layer electrically polymerized on an intermediate Ni plating layer on a Fe sheet specimen [4].

A droplet of a 0.1 M NaCl aqueous solution was put on the bare metal surface of the Fe sheet specimen and the hydrogen entry behavior was visualized in situ on the opposite side of the specimen where the hydrogenochromic sensor was fabricated. In the solution, 50 mM of thymol blue was added to indicate pH distribution.

When the corrosion initiated, the yellowish domain and blueish domain appeared indicating that the separation of anodic and cathodic regions were separated (Fig. 1). The color change to blue is thought to be due to alkalization owing to oxygen reduction reaction. During the early stage of corrosion, no obvious hydrogen entry was observed,

though relatively large crystallographic pits were formed. Our investigation showed that the large crystallographic pits barely promoted hydrogen entry, because crystallographic pitting proceeded in a weakly acidic NaCl solution at potentials higher than the electrode potential of the hydrogen evolution reaction.

As corrosion proceeded, the PANI layer color turned brighter blue showing that hydrogen entry was accelerated where an islandlike rust layer was formed. This was attributed to the acidification under the rust layer. The rust layer was thicker in the outer regions than in the center of the rust island because severe corrosion and alkalization occurred near the oxygen-reductionreaction sites, and dissolved O<sub>2</sub> was readily supplied under the thin solution layer, promoting the generation of oxyhydroxide and hydroxide of Fe ions.

The thick rust layer contained a high concentration of chloride ions, which presumably continuously promoted corrosion and resulting hydrogen entry for a long time, even after the disappearance of the droplet. Consequently, the amount of hydrogen that entered the Fe sheet under the thick rust layer was greater than that under the thin rust layer.

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Fig. 1 Optical images of corrosion side and hydrogen visualization side using a 0.1 M NaCI-50 mM thymol blue. The red arrow indicates the initiation site of corrosion.

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## Regarding Bubbles Produced by Applying Ultrasound to Carbonated Water

In general, microbubbles are defined as those larger than 1  $\mu$ m and nanobubbles as those smaller than 1  $\mu$ m, depending on the difference in particle size of the bubbles, and there are different methods of producing them.

In terms of functionality, microbubbles slowly rise to the surface and disappear in the water, whereas nanobubbles do not rise to the surface and remain suspended in the water. Therefore, nanobubbles have an extremely long lifetime. Furthermore, due to their high internal energy content and high surface charge, nanobubbles have properties and functions that are very different from those of bubbles larger than microns. However, there are still some unresolved aspects of their properties and functions. Microbubbles have also been shown to have a bactericidal effect and there are reports that reactive oxygen species are a part of this mechanism [1]. In previous studies, developed a simple method for generating nanobubbles, using porous alumina films with ordered straight nanoscale size holes. Porous alumina films used as the gas filter in this study were formed by anodization. However, although that method is suitable for generating nanobubble encapsulating various gases, it has difficulty producing a large amount of highly concentrated nanobubbles suspension. This study reports that ultrasound irradiation of carbonated water efficiently can produce nanobubbles containing CO<sub>2</sub> [2].

A beaker was used as a vessel for preparing the nanobubbles suspension, and 200 mL of ultrapure water was placed in it. A commercially available ultrasonic atomization unit was used. The beaker was placed on a commercially available Peltier element-driven cooling plate to maintain the sample temperature below 40 °C.

The ultrapure water was obtained from an ultrapure water purification system, and it contained 8.0-8.3 mg/L dissolved O<sub>2</sub> and 0.26 mg/L dissolved CO<sub>2</sub>.

This water was converted to carbonated water by bubbling CO<sub>2</sub> from a gas cylinder through a gas injector. After bubbling, the concentration of dissolved CO<sub>2</sub> was  $2 \times 10^3 - 4 \times 10^3$  mg/L, and the exact concentration was adjusted through the bubbling time. Next, the carbonated water was irradiated using the ultrasonic atomization unit



Fig.1 Typical size distributions of nanobubbles in the prepared suspension.

described above. The size and concentration of bubbles in the prepared suspensions were measured by nanoparticle tracking analysis (Fig.1). This method has been widely used in recent years to obtain the size and concentration of nanoparticles.

As a result, the bubbles produced in this study were confirmed to be nanobubbles by a nanoparticle characterization system.

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## Energy-Related Materials

IMR KINKEN Research Highlights 2025



#### International Co-Authored Paper

## Growth Kinetics at Vicinal {111} Solid-Liquid Interface of Si

Kinetics at the solid-liquid interface of the vicinal {111} planes of Si was revealed by in-situ experiments. The growth velocity-undercooling relationship was linear, showing that the vicinal {111} planes grow in a step-flow mode.

The {111} planes of Si is known to be an atomically smooth "facet" but the growth kinetics at the solidliquid interface are still under debate. In addition, there have been no experimental observations of the growth of vicinal {111} planes slightly tilted from the {111} plane. In this study, we succeeded in directly observing the growth behavior of vicinal {111} planes and showed that they grow in a step-flow mode [1].

Experiments were conducted using an in-situ observation system consisting of an optical microscope and a furnace. Two Si wafers (20 mm x 5 mm x 0.625) with crystal orientations of <100>, <110>, and <111> along the growth direction were used. The combinations of two wafers were (110)/(111), (100)/(111), and (100)/ (110), each placed side by side between two silica plates. The wafers were partially melted while maintaining a constant temperature until the solid-liquid interface stabilized. The heater was then cooled at 25 K/min or 40 K/min while maintaining the temperature gradient in the furnace at 67 K/cm.

Figure 1 shows the snapshots of (110)/(111) crystal-melt interface cooled at 25K/min. The solidification began at t = 0 s with a curved crystal-melt interface due to non-axial heat flux relative to the crucible. Approximately 10 s into solidification, a small flat facet (marked by a white line in the magnified image) appeared on the {111} interface, emerging from the grain boundary. A white dashed line in the magnified image extends from this flat facet plane. The small flat facet plane deviated from the originally curved plane by a slight angle, suggesting that the initial curved interface was not perfectly aligned with the {111} crystal plane, i.e., it was in the vicinity of the {111} plane (vicinal {111} plane). Similar experiments were performed multiple times with different combinations of wafer orientations and cooling rates. The growth rate of the vicinal {111} plane was measured, and the degree of undercooling was estimated from the analysis of the temperature gradient in the furnace and interface migration.

Figure 2 plots the growth velocity (*V*) vs. degree of undercooling ( $\Delta T$ ) for the vicinal {111} plane. For comparison, values from the two-dimensional (2D) nucleation and dislocation models are also shown in the curves. Large growth velocities are observed even at lower undercoolings, which does not agree with the 2D nucleation law. Furthermore, these values don't



Fig. 1 Video snapshots of (110)/(111) growth at cooling rate of 25 K/min.



Fig. 2 Undercooling vs growth velocity, for all experiments. The 2D nucleation and dislocation kinetic laws are also shown.

align with the dislocation kinetic law, instead displaying a linear relationship between the undercooling and growth velocity. The linear trend observed in Figure 2 leads to the conclusion that all observed vicinal {111} planes follow the step-flow mode given by

$$V = h \frac{\beta}{l} \Delta T, \qquad (1)$$

where *h* is the step height,  $\beta$  is the step kinetic coefficient, *l* is the terrace length and  $\Delta T$  is the undercooling at the vicinal planes. We also discussed in the paper the terrace lengths of the vicinal {111} planes [1].

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## Oxide Particles in Oxide Dispersion Strengthened Steel Neutron-Irradiated up to 158 Dpa

We investigated the stability of oxide nano-particles in oxide dispersion-strengthened steel under neutron irradiation at high temperature to high doses. Almost no change in the morphology of the Y-Ti-O oxide particles has been observed even after being neutron irradiated to high dose of ~160 dpa at high temperature up to 700 °C, which shows stability of the oxide particles under severe irradiation conditions.

Oxide dispersion strengthened (ODS) steels are promising structural materials for next-generation reactor systems. To investigate the resistance of ODS steel under severe irradiation conditions such as high irradiation dose and high temperature, it is necessary to examine the behavior of oxide particles under these severe irradiation conditions. In this study, the stability of the oxide particles in a commercial ferritic ODS steel, MA957, after high neutron dose, up to 158 dpa (displacement per atom) at the fast-neutron experimental reactor JOYO, is studied with three-dimensional atom probe (3D-AP) [1]. Hardness before and after irradiation is also measured to investigate the irradiation effect on mechanical property.

Figure 1 shows atom maps for Cr, Ti, Y, O, TiO, and YO obtained with 3D-AP. Both in the unirradiated and the irradiated samples, a high number density of oxide particle was observed. Cr distribution was almost homogeneous in all the samples, indicating no phase-separation after irradiation. With 3D-AP results, the morphologies of the oxide particles were analyzed by cluster analysis.

For cluster analysis results, no apparent change from the unirradiated sample was found in the sample of 130 dpa at 502 °C and the sample of 154 dpa at 589 °C. In the sample of 158 dpa at 709 °C, the total number density was slightly decreased, and the size distribution became narrower than the that in the unirradiated sample. In addition, the large particles with diameter, d, of >4 nm disappeared, implying that some large particles have been dissolved in the sample of 158 dpa at 709 °C. However, average diameter of the oxide particles did not change significantly with the irradiation

The hardness in the irradiated samples were the same as that of the unirradiated sample, indicating that sufficient mechanical strength was maintained even after high dose at high temperature

To summarize the above, the oxide particles are very stable even after the severe condition of neutron irradiation, to the dose of 158 dpa at 709 °C.



Fig. 1 3D-AP observation for oxide particles; (a) Unirradiated sample, (b) Sample irradiated to 130 dpa at 502 °C, (c) Sample irradiated to 154 dpa at 589 °C, (d) Sample irradiated to 158 dpa at 709 °C.

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#### GIMRT

### Ultrafine YSZ Nanoparticles Dispersed in Zr-Added ODS-Cu Alloy

Gu alloys with high durability and high thermal and electric conductivities are the key to achieving a more energetically efficient and eco-friendly future including the realization of fusion reactors. Noble Zr-added oxide-dispersion-strengthened Cu alloys (ODS-Cu) with high strengths are promising materials for meeting all future service requirements. In this study, the morphology of the oxide particles in the Zr-added ODS-Cu was clarified by small-angle X-ray scattering (SAXS), three-dimensional atom probe (3D-AP), and transmission electron microscopy (TEM).

Materials resistant to extreme environments such as oxide dispersion strengthened (ODS) alloys [1-5], ceramics [6] and heavy alloys [7] are crucial for realizing advanced nuclear systems, such as Gen IV fission reactors and fusion reactors.

ODS-Cu are promising materials for meeting all service requirements because they maintain high strength and extreme durability in harsh environments, especially in fusion reactors where the materials are exposed to high heat fluxes, repetitive stresses, and irradiation environments. In this study, nano-oxide particles in Zr-added Cu-Y2O3 ODS alloys were analyzed on a multiscale using SAXS, 3D-AP, and TEM to reveal their composition, formation mechanism, and dispersion [1]. In Zr-added Cu-Y2O3, Zrrich YSZ, which has not been reported in other Zr-added ODS alloys, was mostly formed as nano-oxide particles, as shown in the 3D-AP results (Fig. 1). The high interfacial coherency between the YSZ nano-oxide particles and the Cu matrix (Fig. 2) is considered to be the reason for the formation of the fine YSZ particles. However, multiscale analysis using SAXS and 3D-AP revealed inhomogeneous nano-oxide particle dispersion in the Zr-added Cu-Y2O3. As the specimen size increased, the observed number density of nano-oxide particles decreased. This suggests that there are microstructures with dense and sparse nanooxide particles in the Zr-added Cu-Y2O3 due to the MA inhomogeneity. Homogenization of the nano-oxide particle dispersion leads to a further increase in the strength of the Zr-added Cu-Y<sub>2</sub>O<sub>3</sub>. Various types of ODS alloys such as Al-added high Mn austenite ODS steel and ODS-Co were also fabricated and examined to achieve excellent properties against severe environments [2-5].

Tungsten materials shows room temperature brittleness but their notable physical properties, such as its high melting point, strength, thermal conductivities, and low spattering yield, make it an attractive candidate for various applications particularly as a plasma-facing structural material in fusion reactors. We conducted a detailed characterization of the fracture behavior of cold rolled W using the 3D-EBSD technique and micro-bending tests at RT, suggesting that the presence of low-angle grain boundaries in the cold rolled W can enhance dislocation mobility and accommodate dislocations emitted from the crack tip, thereby improving ductility [7].



Fig. 1 Atom maps of the 3D-AP specimens containing Y-Zr nanooxide particles [1].



Fig. 2 Coherency of the YSZ nano-oxide particle and the Cu matrix [1].

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## Oxide Crystal Growth From Cold Crucible: Melt Growth Method Without Using Precious Metal Crucibles

A new method for growing oxide single crystals with higher purity and lower defects than conventional methods, OCCC method, is introduced. Some of the OCCC grown Ce:GAGG showed  $\gamma$ -ray excited light yield and decay time comparable to those of commercial crystals.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals of approximately 2-inch diameter have also successfully grown by this method. The obtained  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals were of high purity, and only impurities of raw material origin were detected. The full width at half maximum of the X-ray rocking curve was comparable to that of commercial  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.

In the history of mankind, "civilizational innovations" have always been brought by the "emergence of new materials and the practical application of new materials with higher purity, lower defects, and defect control". Civilizations have improved as materials have become more sophisticated. From vacuum tubes to transistors, silicon semiconductor crystals became highly purified and less defective, and in no time at all, silicon transistors were put to practical use, replacing vacuum tubes. In the field of LEDs, the p-type GaN pioneered the blue LED, and the low-defect technology of GaN succeeded in extending the life of LEDs, which was put into practical use and replaced the light bulb in no time. As history has shown, the "method" to realize "the emergence of new materials and the practical application of new materials through high purity, low defects, and defect control" is also important, and we are conducting research for contributing to the above. In this paper, we introduce a single crystal growth method for oxide that enables much higher purity, lower defect counts, and easier defect control compared to conventional methods. We call this method oxide crystal growth from cold crucible (OCCC) method.

Here two examples were present: Ce doped Gd<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub> (Ce:GAGG), a scintillator with the highest light yield among the oxides, developed in our laboratory, and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, which is a next-generation power semiconductor.

Bulk single crystal of Ce:GAGG were grown from the melt using OCCC method [1]. Although this was an early trial in which all the growth condition was not optimized, the photoluminescence and radioluminescence spectra of the obtained Ce:GAGG crystals were very similar to those of commercial Ce:GAGG, peaking attributable to the 5d1–4f transition of Ce<sup>3+</sup>. Moreover, during the  $\gamma$ -ray-excited light yield and decay time measurements, some of the samples showed values comparable to those of the commercial Ce:GAGG reference sample.

Melt growth of bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals (Fig. 1) by OCCC method was also succeeded [2]. The absence of an expensive precious-metal crucible makes this a cost-effective crystal growth method, which is a critical factor



Fig.1 (a)Schematic of OCCC method. (b)Photo of β-Ga2O3 crystal grown by the OCCC method.

in the semiconductor industry [3]. An original construction 0.4-0.5 MHz SiC MOSFET transistor generator with power up to 35 kW was used to successfully grow bulk β-Ga<sub>2</sub>O<sub>3</sub> crystals with diameters up to 46 mm. Even in this preliminary study, the full width at half maximum of the X-ray rocking curve obtained from the β-Ga<sub>2</sub>O<sub>3</sub> crystals with diameters  $\leq$  46 mm was comparable to those of commercial β-Ga<sub>2</sub>O<sub>3</sub>. As expected, the purity of the obtained crystals was high as only raw materialderived impurities were detected. Technoeconomic modeling results [3] showed that the cost of iridium (used as the crucible material) is the major factor determining the total cost of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> wafer. Therefore, Reese et al. [3] suggest that technological innovations - such as the development of alternative crucible materials that can significantly lower the cost of β-Ga<sub>2</sub>O<sub>3</sub> substrates - can encourage the widespread use of gallium oxide semiconductor devices. Since the release of this analysis, the price of iridium has increased by more than 3 times! Our results indicate that the OCCC method can be one of the strongest candidates to fulfill the requirement of this analysis.

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## Structural Analysis of Ca9RE(PO4)7 (RE = Eu or Er ) Phosphors

he structures of Ca<sub>9</sub>Eu(PO<sub>4</sub>)<sub>7</sub> and Ca<sub>9</sub>Er(PO<sub>4</sub>)<sub>7</sub> phosphors were analyzed using single-crystal X-ray diffraction. Most Eu reside at the medium-sized M1 and M2 sites, with a small amount occupying the M5 site. In contrast, the smaller Er favor the smallest M5 site. This study also demonstrates the use of anomalous X-ray scattering measurements at the Er L<sub>III</sub> and Er L<sub>III</sub>-edges. The energy dependencies observed in the scattering factors for Ca<sub>9</sub>Eu(PO<sub>4</sub>)<sub>7</sub> and Ca<sub>9</sub>Er(PO<sub>4</sub>)<sub>7</sub> confirmed the preferred distribution of Eu and Er [1].

The characterization of luminescent materials has attracted considerable attention because solid-state lighting systems with luminescent materials offer advantages over fluorescent and incandescent lights. A variety of RE-substituted phosphate crystals have been reported for their superior structural compatibility with the substitution of rare-earth elements. Among the available host crystals, rare earth-substituted  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is of special interest. The relationships between the location of the rear-earth activator and the optical properties are important issues in materials science. Anomalous X-ray scattering is an advanced diffraction method that allows for the analysis of the environmental structure around a specific element.

AXS measurements for the Eu and Er Lui-absorption edges were performed at the Photon Factory (PF) BL-6C, Institute of Material Structure Science (IMSS), High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. A pair of incident energies corresponding to 25 and 100 eV below each LIII absorption edge (Eu: and Er) was used in the AXS measurements. These energies were well tuned by employing a Si (111) monochromator. A transmission-type phase retarder of (100) diamond was used to transform the linear polarization of the synchrotron radiation into a circular polarization via dynamic diffraction. The combination of a  $\kappa$ -goniometer and HCP detector of Synergy-AXS enabled the fast acquisition of single-crystal diffraction data sets.

The Ca<sub>9</sub>RE(PO<sub>4</sub>)<sub>7</sub> compounds (RE = trivalent rear earth elements) crystallized in the space group *R*3<sub>c</sub>. The crystallized structure, shown in Fig. 1, is characterized by four large cation sites for Ca and RE, three P sites tetrahedrally coordinated to four oxygen atoms, and ten independent oxygen sites. A variety of cations with different valence states and sizes can occupy the four distinct sites, M1, M2, M3, and M5, with coordination numbers ranging from 6 to 8. The present structural analysis indicates that the medium-sized Eu prefers the M1 and M2 sites with coordination numbers of seven, whereas the smaller Er prefers the smallest M5 site with a coordination number of six, which is usually occupied by Mg and Mn in hydrous whitlockite with similar structural features.

Figure 2 shows the comparison between the experimental values  $(IF-100eVI^2 / IF-25eVI^2)_{exp.}$  and  $(IF-100eVI^2 / IF-25eVI^2)_{cal.}$  calculated from the results of structural analysis for Ca9Eu(PO4)7. Although the number of measured reflection intensity was insufficient due to the limited beam time, the overall agreement between the measured and calculated



Fig. 1 The structure of Ca9RE(PO4)7



Fig. 2 The AXS analysis for Ca9Eu(PO4)7 at the Eu LIII-edge.

intensity variations suggests the feasibility of the distribution model obtained in this study. These results are consistent with those obtained from powder diffraction reports [2], including the significant amount of smaller Er associated with the lanthanoid contraction rule also residing at medium-sized M1 and M2 sites.

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## Unlocking the Potential of Next-Generation Oxide Cathodes for Rechargeable Magnesium Batteries

Rechargeable magnesium batteries (RMBs) promise sustainable energy solutions due to magnesium's abundance and high energy density. However, overcoming challenges related to cathode materials has remained critical. Our research has advanced the understanding of high-entropy (HE) disordered rocksalt oxides and delithiation-induced amorphous oxides, addressing key barriers to RMB development.

#### **High-Entropy Oxide Cathodes**

The rocksalt structure has traditionally been regarded as unsuitable for cathodes in RMBs due to its densely packed cations, which severely hinder Mg diffusion. Consequently, prior studies aimed to avoid the formation of rocksalt phases, favoring spinel structures that offer lower energy barriers for Mg migration and operate at elevated temperatures of around 150 °C. Departing from this conventional approach, we developed a high-entropy disordered rocksalt oxide, Mg0.35Lio.3Cro.1Mn0.05Fe0.05Zn0.05M00.1O (M7O), as a cathode material for RMBs [1].

The cation vacancies, created by the initial Li extraction cycle, secure the Mg migration path by significantly decreasing its energy barrier. This allows reversible Mg insertion and extraction at an operational temperature of 90 °C, substantially lower than the temperature required for conventional spinel oxides. These findings challenge long-standing assumptions about the limitations of rocksalt structures in RMBs and highlight the potential of vacancy-driven design strategies for developing advanced oxide cathodes.

#### **Amorphous Oxide Cathodes**

Inspired by the insights from the rocksalt oxide cathode, we explored how delithiation-induced cation vacancies could further enhance Mg migration. We developed Li<sub>2</sub>Ti<sub>1</sub>/<sub>3</sub>Mo<sub>2</sub>/<sub>3</sub>O<sub>3</sub> [2], a composition specifically designed to increase cation vacancies through Li extraction. Interestingly, the material transformed into a composite dominated by an amorphous phase with a minor disordered rocksalt phase upon delithiation. Despite this structural change, the amorphous material demonstrated substantial activity for Mg insertion and extraction, enabling operation at a near-room temperature of 60 °C.

The redox activity of Mo<sup>4+/6+</sup> facilitates Mg accommodation, while the large free volume introduced by Li extraction supports efficient Mg diffusion. These results suggest that amorphous materials represent a novel family of oxide cathodes,







Fig. (a) SEM-EDS images of M7O [1]. The scale bar is 10 μm. (b) Schematic of charging/discharging mechanism in the amorphous oxide cathodes [2].

significantly broadening the scope for designing RMBs capable of practical operation at or near room temperature. This advancement provides a pathway toward untapped oxide cathodes for RMBs. Eventually, it aligns with the increasing demand for efficient and versatile energy storage solutions by addressing the challenges in rechargeable batteries.

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#### International Co-Authored Paper

## Mechanically Robust Self-Organized Crack-Free Nanocellular Graphene with Outstanding Electrochemical Properties in Sodium Ion Battery

Nanocellular graphene (NCG) is a new type of graphene-based three-dimensional bulk material with a large specific surface area. NCGs have attracted much attention as a material for high-performance energy devices because of their excellent properties derived from graphene combined with a cellular structure. We have successfully developed a new method for the synthesis of large crack-free NCGs based on liquid metal dealloying (LMD) technology. The developed NCGs exhibit high rate, long life, and excellent deformation resistance as electrodes for sodium-ion secondary batteries (SIBs), enabling high performance and flexibility of SIBs.

The demand for wearable electronic devices with IoT functions, especially in medical and nursing care applications, has resulted in a need for flexible rechargeable batteries. Conventional electrodes used in the batteries, which consist of graphite particles bonded to a metal current collector, are not flexible and can experience issues such as detachment of active material from the collector. To address this, a sheet-type carbon material with excellent mechanical and electrochemical properties was needed.

Nanocellular graphene (NCG) is a new type of graphene-based three-dimensional bulk material that achieves a large specific surface area by stacking multiple layers of graphene and controlling the internal structure with a cellular morphology. NCG is attracting attention as it has the potential to improve the performance of electronic devices, energy devices, etc. However, cracking is inevitable during fabrication using conventional processes, which significantly reduces the desirable properties of NCGs. Therefore, it is difficult to fabricate homogeneous and crack-free seamless NCGs on a large scale.

To solve this problem, we have developed a new fabrication process for NCGs by liquid metal dealloying (LMD) using amorphous carbide precursors [1]. Since amorphous materials has a long-range homogeneous structure without grain boundaries, cracks can be prevented during NCG formation, as schematically shown in Fig.1(a).

Mn80C20 (at.%) thin films were deposited by sputtering method and their amorphous structure was confirmed by X-ray diffraction. The amorphous Mn-C precursor film was subjected to LMD in a Bi bath to selectively leach Mn atoms and self-assemble C atoms into a seamless NCG. Figure 1(b, c) shows the cross section of a sample that was LMDed at 1273 K for 3 min. The sample has a sheet shape and its interior has a cellular structure consisting of seamlessly connected nano-sized hollow cells. It also shows good flexibility as shown in Fig. 1(d). The Raman spectrum measured from the sample is shown in Fig. 1(e). The strong G band and 2D band are observed, indicating the formation of highly crystalline graphene. The electrical conductivity and fracture strength of NCG reached  $1.6 \times 10^4$  S/m and 34.8 MPa, respectively, both of which are top level compared to other cellular graphene materials.



Fig.1 (a) Schematic illustration of the LMD reaction during which the selective dissolution of Mn into molten Bi and the self-organization of C at the solid–liquid interfaces lead to the formation of NCG. (b,c) Cross-sectional SEM images of the crack-free NCG synthesized at 1273 K for 3 min. (d) Photograph of the flexible freestanding NCG film. (e) Raman spectra of the as-produced and 2500 °C-graphitized NCG. (f) Cycling tests of a NCG-based pouch battery at different current densities (1, 5, and 20 A g<sup>-1</sup>) and states (flat, bent to a radius of 1 or 0.75 cm).

The performance of the developed NCG as an electrode for sodium ion batteries (SIBs) was evaluated. It showed larger mass-specific capacity and better rate performance compared to artificial graphite. The cyclic tests at a current density of 5 A/g showed that NCG maintained 100% coulombic efficiency after 7,000 cycles, indicating good stability. Figure 1(f) presents the effect of NCG electrode deformation on electrode properties. It shows identical capacity under both flat and bent (radius of curvature 0.75 cm and 1.0 cm) conditions at current density 5 A/g and 20 A/g. Thus it is concluded that the developed NCG are useful for enhancing electrochemical performance and flexibility of SIBs.

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## Quantitative Evaluation of Figure of Merit for Transverse Thermoelectric Conversion in Fe/Pt Metallic Superlattices

ransverse thermoelectric conversion, driven by the anomalous Nernst effect in magnetic materials, offers simplified structures for applications, and attracts much attention as an efficient energy harvesting technique. We developed a novel method to evaluate the transverse thermoelectric figure of merit zT in thin films and applied it to Fe/Pt superlattices. Our method clarified that a larger repetition number and the epitaxial growth of superlattice significantly enhance zT.

Transverse thermoelectric conversion, in which a temperature gradient induces a transverse electric field, represents a promising avenue for next-generation energy harvesting technologies. Unlike conventional longitudinal thermoelectric systems, transverse thermoelectric devices offer simpler structures and enhanced thermal energy harvesting efficiency due to minimized electrical and thermal contact resistance. Among transverse thermoelectric effects, the anomalous Nernst effect (ANE) in magnetic materials stands out as a key phenomenon. The performance of transverse thermoelectric conversion for ANE is characterized using the figure of merit  $zTT = ST^2 \sigma_{yy} T/\kappa_{xx}$ , where ST,  $\sigma_{yy}$ ,  $\kappa_{xx}$ , and T denote the transverse thermoelectric coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Previous studies have demonstrated that metallic superlattices can enhance  $S_T$  [1, 2]. In addition, the inherent structural anisotropy of superlattices, as illustrated in Fig. 1(a), holds potential to reduce out-of-plane  $\kappa_{XX}$  while maintaining in-plane  $\sigma_{VV}$ , leading to an enhancement of zTT. Despite these advantages, a reliable method to evaluate zTT in thin films, including superlattices, had not been established.

To address this challenge, we proposed and demonstrated a novel methodology for accurately evaluating  $z\tau T$  in thin-film forms [3]. Our approach involves measuring  $\kappa_{XX}$ , ST, and  $\sigma_{YY}$  using the timedomain thermoreflectance, the heat flux method, and the four-terminal method, respectively. This technique was applied to epitaxial and polycrystalline Fe/Pt superlattices with varying stacking repetitions N. The high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images indicated that all the Fe/Pt superlattices successfully formed layer stackings with clear interfaces [inset of Fig. 1(b)]. We systematically investigated the dependence of  $\kappa_{XX}$ , ST, and  $\sigma_{YY}$  on N, and evaluated ZT using three parameters. We found that the superlattice structure effectively suppresses  $\kappa_{XX}$ , while ST drastically increases with increasing N, resulting in a significant enhancement of zTT as shown in Fig. 1(b). Furthermore, we clarified epitaxial superlattices have higher transverse





thermoelectric conversion performance than polycrystalline superlattices. This study represents a pioneering effort in the evaluation of  $z_TT$  in thin-film forms. Our proposed method will provide design guidelines for thin film materials that exhibit high transverse thermoelectric conversion performance. We anticipate that this approach will accelerate materials research in thermoelectricity and spin caloritronics, paving the way to advanced energy harvesting solutions.

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#### GIMRT International Co-Authored Paper

## Hydrogen Absorption Reactions of a New AB<sub>3</sub>-Based Alloy

Hydrogen storage materials, which store hydrogen as atomic state, have great advantages as compact hydrogen storage methods compared with gaseous and liquid hydrogen. By contrast, improvement of gravimetric hydrogen density is a key issue for their developments. Herein, we show hydrogen absorption reactions on a new AB3-based alloy, Y0.68Mg0.32Co3.00, with a gravimetric hydrogen density of 1.68 mass% and reversible hydrogen absorption reactions at 303 K. Interestingly, the gravimetric hydrogen density was increased up to 2.88 mass% at 10 GPa.

Hydrogen stored as gaseous, liquid, and solidstate could be one important technology in the hydrogen-based society. The solid-state hydrogen storage is so-called hydrogen storage materials, which store hydrogen as atomic states and compacter hydrogen storage methods than gaseous and liquid hydrogen. By contrast, improvement of hydrogen storage capacity per total weight (i.e. gravimetric hydrogen densities) is a key issue for their developments.

Intermetallic compounds AB2, AB3, and AB5, in which components A and B are elements from groups 1-5 and 6-12 of the periodic table, are typical hydrogen storage materials. We reported AB2-based alloys (Y, Mg)(Co, Ni)<sub>2</sub>, which were synthesized from YCo<sub>2</sub> and MgNi<sub>2</sub> [1]. In the results, their hydrogen absorption and desorption pressures and gravimetric hydrogen densities were depended on amounts of Mg and Co. To improve the gravimetric hydrogen density, YCo2 and MgCo<sub>2</sub> were used as starting materials for the synthesis. Resulting that, a new AB3-based alloy, Y0.68Mg0.32Co3.00, was yielded instead of (Y, Mg)Co2 [2]. Y0.68Mg0.32Co3.00 exhibited reversible hydrogen absorption and desorption reactions with a gravimetric hydrogen density of 1.68 mass% below 10 MPa at 303 K. The gravimetric hydrogen density was higher than those of (Y, Mg)(Co, Ni)2 and an industrially used material LaNi5. Furthermore, hydrogen (deuterium) atomic positions in Y0.68Mg0.32C3.00 during the hydrogen absorption reaction were clarified by X-ray and neutron diffraction experiments (Fig. 1).

Although hydrogen storage properties are usually investigated below 10 MPa, reactions between hydrogen and materials are proceeded above 1 GPa since hydrogen chemical potential is increased. This suggests that the high-pressure experiments above 1 GPa lead to obtain insight into improvements of gravimetric hydrogen densities. Therefore, we observed hydrogen absorption reaction of Y0.68Mg0.32Co3.00 above 1 GPa at room temperature. Considering on unit cell expansions of Y0.68 Mg0.32 Co3.00, the gravimetric hydrogen density was estimated to



Fig. 1 (a) Crystal structure and local atomic arrangements of deuterium absorbed Y0.68Mg0.32C3.00, and (b) hydrogen absorption reaction of Y0.68Mg0.32C03.00 below 10 GPa.

reach 2.88 mass% at 10 GPa (Fig. 1).

This indicates that Y0.68Mg0.32Co3.00 has a potential to be a candidate of hydrogen storage material with a high gravimetric hydrogen density.

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## First-Principles Investigation of Point Defects in Low-Dimensional Semiconductor Materials

Low-dimensional materials, including layered materials and their exfoliated two-dimensional (2D) counterparts, have attracted significant attention due to their potential in advanced electronics, catalysis, energy storage, sensing, and quantum computing. Point defects play a pivotal role in determining their electrical, ionic, and photocatalytic properties, and first-principles calculations have been increasingly employed to investigate dominant point defects in 2D materials. Nevertheless, the number of such studies remains comparatively limited when contrasted with research on three-dimensional (3D) materials. To overcome the situation, in this series of studies, we have developed a methodology and computer program to accurately and automatically calculate point defect formation energies in 2D materials. We have applied this approach to high-throughput calculations on impurities in MoS<sub>2</sub> and to exploring the p-type dopability of layered  $\beta$ -TeO<sub>2</sub>.

Low-dimensional, layered materials, including their 2D forms, are promising for advanced electronics, catalysis, energy storage, sensing, and quantum computing. Point defects critically influence their properties, yet first-principles studies remain limited compared to 3D systems.

To overcome the situation, we developed a method to automatically and effectively calculate accurate defect formation energies in 2D materials and implemented it in pydefect\_2d code [1]. Furthermore, we explored the impact of ill-defined dielectric profiles on the corrections and demonstrate that the selection of the profiles potentially affects the corrections for defects far from the surfaces significantly.

We then applied it to study the elemental doping in the monolayer MoS<sub>2</sub> [2]. We identified thermally stable sites of 27 elemental dopants, along with their formation energies and charge transition levels. Consequently, we found that the polaronic states are universally stable with deep transitions located 1.0 eV away from the band edges, which remains even with substrates. Our study offers fundamental insights into elemental doping in MoS<sub>2</sub> and similar 2D semiconductors

We also calculated the native defects and impurities in  $\beta$ -TeO<sub>2</sub> [3, 4]. The exfoliated 2D  $\beta$ -TeO<sub>2</sub> has gained attention as a promising material for optoelectronic and power device applications. We investigated the intrinsic and extrinsic point defects in 2D and 3D  $\beta$ -TeO<sub>2</sub>. Our results have revealed that most intrinsic defects are unlikely to contribute to p-type doping in 2D β-TeO<sub>2</sub>. Moreover, Si contamination could further impair p-type conductivity. We also explored substitutional p-type doping in 2D  $\beta$ -TeO<sub>2</sub> with various trivalent elements. Among these, the Bi dopant is found to exhibit a relatively shallow acceptor transition level. However,





most dopants tend to introduce deep localized states, where hole polarons become trapped at Te's lone pairs. Similar behavior is also observed in 3D  $\beta$ -TeO<sub>2</sub>.

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## Electronic Materials

IMR KINKEN Research Highlights 2025

#### International Co-Authored Paper

## Quantifying the Progress of Numerical Simulations in Solving Quantum Many-Body Problems

Lunctional properties of materials such as superconductivity and magnetism arise from complex quantum mechanical interactions between interacting electrons. Numerical simulations of quantum many-body problems are rapidly gaining importance in predicting such functional properties. In this study, we quantify the frontier of such numerical simulations, visualize the degree of progress of numerical methods on classical computers, and clearly defines the target of quantum computation toward the quantum advantage.

The quantum many-body problem is a challenging and fascinating problem that aims to achieve the ultimate understanding of various phenomena by describing emergent properties arising from interactions among elementary particles. An electron is one such elementary particle, and it is indispensable to analyze quantum many-body problems of electrons to understand and predict material properties.

Recently, research using computer simulation has made great progress in solving this difficult problem. For example, attempts have been made to quantum mechanical solve the equation (Schrödinger equation) using supercomputers such as "Fugaku" and various state-of-the-art computational methods including methods based on machine learning [1] to elucidate hightemperature superconductivity and exotic quantum phenomena. Furthermore, on top of the simulations using classical computers, simulations using quantum computers have started to attract keen attention as a new and promising computational technique.

In the midst of this competition, it has emerged as a very important issue to quantify the frontiers of numerical methods for quantum many-body problems, to create a unified metric for comparing the performance of various computational methods, and to clarify the criteria for the "quantum advantage" of quantum computers over classical computers.

In this study, research groups operating stateof-the-art numerical computation techniques collaborated internationally to collect results of quantum many-body problems solved by different state-of-the-art methods and proposed a unified metric (V-score) that represents the accuracy of the results [2]. By quantifying the accuracy, the degree of progress of numerical methods for the quantum many-body problem has been visualized. In the quantum many-body problem of predicting material properties, particularly challenging problems for numerical techniques are frustrated quantum spin



Fig. 1 List of accuracy metric V-score for quantum manybody problem analyses. Texts outside the circles indicate the type of quantum many-body problem for predicting physical properties, which differs depending on the crystal structure and the composition of the material. For each problem, the values of the V-score are shown, with smaller (larger) V-score values indicating easier (more difficult) analysis [2].

systems, where the interactions among electron spins become complicated because of the geometry of crystal structure, and strongly correlated electron systems, where the strong electron interactions give rise to exotic quantum phenomena such as hightemperature superconductivity. These problems should become a target of quantum simulations. Also, the elucidation of the current status of classical simulations clearly defines the criteria for quantum advantage [2].

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#### GIMRT International Co-Authored Paper

## One-Ninth Magnetization Plateau Stabilized by Spin Entanglement in a Kagome Antiferromagnet

In S=1/2 Heisenberg Kagomé lattice antiferromagnet, the strong geometrical frustration is expected to cause many body entangled states. 1/9 magnetization plateau has been explored as the manifestation of such nontrivial states. We found the realization of 1/9 plateau by using pulsed magnetic field magnetization measurement in <sup>3</sup>He temperature for the first time.

In S=1/2 Kagome Heisenberg antiferromagnet, the existence of quantum spin liquid state has been investigated for decades. When strong magnetic fields are applied for the system. fractional magnetization plateaus are observed in m=1/9, 3/9, 5/9, and 7/9, where m=1 is the fraction to the saturation magnetization. The mechanism m=3/9, 5/9, and 7/9 plateaus is the crystallization of magnons. The excitations in hexagon of the Kagome lattice are localized for the strong frustration and the solid of magnon appears at these values of m. These plateau states are stabilized by the excitation gap.

The origin of 1/9 magnetization plateau is considered to be different from other plateaus. It is proposed that the spin entanglement is the mechanism of this non-trivial state. Despite the strong interest for 1/9 magnetization plateau, the realization by experiments has been elusive for the lack of model materials.

The recently discovered new Kagome material YCu<sub>3</sub>(OD)<sub>6+x</sub>Br<sub>3-x</sub> brings the new breakthrough. The system has only tiny site-disorder, but-there is the random distribution of OD–/Br– bonds introducing exchange randomness. Despite the randomness, the system has ideal property as Kagome lattice antiferromagnet and It shows no magnetic ordering down to 50 mK.

We measured magnetization up to 25 T at T=0.5 K by using a pulsed magnetic field setup. In the magnetic field perpendicular to the Kagome plane (H//c), a clear 1/9 magnetization plateau is found. The lower and upper critical fields correspond to 15.4 T and 18.3 T, respectively. For in-plane magnetization curve, 1/9 plateau is also found with a finite slope for anisotropy. The critical fields shift to higher fields 16.8 T and 21.1 T. The anisotropy of critical fields can be explained by g-factor anisotropy in part and the finite slope is not expected in this case. Another cause of the anisotropy is the Dzyaloshinskii-Moriya(DM) interaction. The magnitude of the out of plane DM component is estimated to be 2.2 K and is comparable to the

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Fig. 1 Magnetization curve at 0.5 K and 1/9 magnetization phase [1].

width of the out-of-plane plateau. The DM interaction is the cause of finite slope of in-plane magnetization curve, but the 1/9 magnetization plateau phase is maintained under such term.

We have investigated heat capacity, thermal conductivity, Raman scattering. All experimental data shows that YCu<sub>3</sub>(OD)<sub>6+x</sub>Br<sub>3-x</sub> is a unique Kagome model system. It is found that the 1/9 magnetization state is realized even if there are bond-randomness and the DM interaction. It is also unique that the plateau phase can be accessed by the 25 T superconducting magnet working at high magnetic field laboratory of IMR. A detailed investigation on the nature of quantum entanglement in 1/9 magnetization plateau will open the new understanding of quantum spin liquid and the ground state of Kagome antiferromagnet.

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#### GIMRT

## Molecular Monomer Mott Insulator (BEDT-TTF)Cu[N(CN)2]2

A spin-1/2 (BEDT-TTF)<sup>1+</sup> monomer Mott insulator (BEDT-TTF)Cu[N(CN)<sub>2</sub>]<sub>2</sub> is revealed as a Dirac semimetal with nodal lines at the Fermi level by the band structure calculations. Resistivity and magnetic susceptibility indicate the monomer Mott insulating state instead of the expected semimetal state probably owing to strong electron correlation. In addition, a steep reduction of paramagnetic susceptibility appears below approximately 25 K, which indicates a spin-singlet ground state.

Electronic band structures with linear dispersion have attracted much attention in recent years because of the massless Dirac-like nature of the fermion carriers. When the Fermi level is located near the center of the dispersion, the Dirac semimetal state can be achieved. The discovery of the quantum Hall effect in graphene as a 2D Dirac semimetal with the cone type dispersion has begun to attract many studies. Especially, organic molecular based compounds are good platform to investigate the Dirac semimetal in the bulk system.

Title organic salt (BEDT-TTF)Cu[N(CN)2]2 could be considered as a spin-1/2 BEDT-TTF<sup>1+</sup> (ET<sup>1+</sup>) monomer Mott insulator. In (ET)Cu[N(CN)2]2, a peculiar 3D anisotropic diamond-like network is composed of stacked one dimensional zig-zag chains of ET molecules, which is shown in Fig. 1(a) [1]. The ET molecules form a 1D zigzag chain at regular intervals along the *c*-axis with the nearest intermolecular (diagonally side-by-side) S-S contact (red lines, *t*). There is a two-fold rotation axis perpendicular to the ET molecular plane, which guarantees the 1D chain to be uniform. In addition to the intra-chain coupling, the second-nearest interaction (blue lines, *t'*) connects neighboring chains. Namely all the ET molecules are in distorted tetrahedral coordination geometry.

We revealed that the uniform zigzag chain with inter-chain (anisotropic diamond-like) dihedral interaction gives rise to a potential Dirac semimetal state with nodal lines by investigating band structures calculated by the tight binding model based on the extended Hűckel method and the DFT calculations. There are two band dispersions corresponding to the two equivalent ET molecules. Taking account of one electron transfer from the HOMO of ET to the charge compensating anion, the Fermi level is located at the middle of the HOMO band, resulting in the 1/2-filled band as depicted in Fig. 1(b). This band degeneracy at Z comes from the zigzag uniform chain structure, leading to 1D "nodal" Fermi surfaces on Z with linear energy dispersion at around the 1st BZ.

The present salt has a 1/2-filled band, and thus a most reasonable interpretation of the insulating behavior is the scenario as a Mott insulator by the





strong on-site Coulomb interaction. The localized site should be an ET molecule (monomer) in contrast to dimer-Mott insulators in typical 1/4 filling ET salts. In addition, the paramagnetic insulating electronic properties in the 1/2-filled band is well explained in terms of the Mott insulator [1]. The sudden drop of paramagnetic susceptibility below 25 K indicates a spin-singlet (non-magnetic) ground state [2].

This material is very interesting as a good candidate for the study of Dirac fermions with linearly dispersive bands.

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## Field-Induced Criticality in YbCu4Au

We report on the field-induced criticality of YbCu4Au. Successive transitions below 1 T were observed via specific heat, resistivity, neutron diffraction, and µSR. XAS revealed valence stability above 2 T, attributed to electric quadrupoles. YbCu4Au exhibits a bi-critical point near 1 T.

Research on quantum criticality has been one of the main themes in solid-state physics. Recently, quantum criticality driven by new degrees of freedom beyond spin have attracted attention. In heavy-electron systems with strong Kondo effects, valence fluctuations arise when the repulsion between conduction and *f*-electrons competes with kinetic energy of *f*-electrons, potentially leading to valence quantum criticality. However, candidate materials that host such phenomena remains a challenge.

YbCu4Au is a candidate material where spin and valence fluctuations coexist [1]. Previous studies on polycrystalline samples have reported a magnetic transition from specific heat, resistivity, and Nuclear Magnetic Resonance measurements, with transition disappearing under a magnetic field of 1.3 T. However, magnetostriction have also reported the possibility of an electric quadrupole contribution above 1.3 T, indicating a more complex scenario [2]. Determining the valence state of Yb is critical to resolving this issue.

In this study, we successfully synthesized single crystals of YbCu<sub>4</sub>Au for the first time and investigated their electronic states by X-ray diffraction, neutron powder diffraction, specific heat, resistivity, muon spin relaxation ( $\mu$ SR), and X-ray absorption spectroscopy (XAS). Structural analyses confirmed consistency with previous polycrystalline studies [1]. Specific heat, resistivity, and  $\mu$ SR measurements revealed successive magnetic transitions at  $T_{m1} = 0.66$  K and  $T_{m2} = 0.48$  K below 1 T.

Here, we present the results of XAS measurements aimed at determining the electronic states above 2 T. The temperature dependence of the absorption spectrum under 7 T and the magnetic field dependence of the absorption spectrum at 3 K are shown in Fig. 1(a) and 1(b), respectively. Unlike the distinct changes observed in the case of YbCu4In at various temperatures and magnetic fields, no significant changes were observed in YbCu4Au. Consequently, based on these results, we conclude that YbCu4Au exhibits a valence fluctuation state in the temperature range 3 K < T < 200 K and the magnetic field range 0 T < B < 7 T,



Fig. 1 (a) Temperature dependence of the X-ray absorption spectra of YbCu<sub>4</sub>Au at 7 T. (b) Magnetic field dependence of the absorption spectra at 3 K.

but without a distinct average value of valence change [3].

In conclusion, the magnetic order in YbCu4Au results from the interplay of spin and valence fluctuations, with electric quadrupoles induced above 2 T. Bi-critical point near 1 T is from the competition between magnetic dipole interactions and the Zeeman effect. This study establishes YbCu4Au as a unique system for exploring quantum criticality.

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### **Room Temperature Chirality Control and Detection in a Helimagnet**

In helimagnets, the magnetic moments order spirally. The handedness of helix is an internal degree of freedom denoted as chirality. It seems quite robust against disturbances and is therefore promising for next-generation magnetic memory. Here we demonstrate the control of chirality at room temperature in a helimagnetic MnAu2 thin-film. In addition, we have succeeded in detecting the chirality at zero magnetic fields by means of simple transverse resistance measurement.

Spintronics based on antiferromagnets is currently attracting considerable attention. A helical magnet is one form of antiferromagnet that has unique characteristics: Mirror symmetry is broken, and the chirality works as an internal degree of freedom unless the crystal structure is noncentrosymmetric. The chirality does not couple to the magnetic field and is invariant under any translation and rotation. In order to reverse it, one has to first straighten the spin direction and wind it reversely. In other words, the helimagnetic memory is topologically protected in that way and should be stable even in a very small device. Therefore, this seems to be a desirable degree of freedom for nextgeneration magnetic storage.

In this work, we show room temperature chirality control in a thin film MnAu<sub>2</sub> helimagnet by applying an electric current in a magnetic field. The chiral degeneracy is lifted by the magnetic field and electric current owing to the effect of spin transfer torque as shown in Fig. 1. Figure 2 shows the nonreciprocal resistivity  $\rho_{asym}^{2\omega}$  measured after the chirality control by the magnetic field sweep from  $H_0=\pm 3T$  with the application of electric current  $j_0=0$ ,  $\pm 8.0 \times 10^9$  A/m<sup>2</sup>.  $\rho_{asym}^{2\omega}$  is the field-asymmetric component of second harmonic resistivity and is known to probe the sign of chirality. While  $\rho_{asym}^{2\omega}$  was almost negligible for  $j_0=0$ , finite  $\rho_{asym}^{2\omega}$  was observed for the other data. The sign depends on whether Ho and jo are parallel or antiparallel, demonstrating that the chirality was controlled successfully.

We also show the chirality can be probed by the transverse resistance at zero magnetic fields in a bilayer device composed of MnAu<sub>2</sub> and a spin Hall material Pt, which originates from the spin Berry phase [1].

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Fig. 1 Schematic illustration of the chirality control [1]. The chirality is controlled by the electric current *j* and the magnetic field *H*, depending on whether *j* and *H* are parallel or antiparallel.



Fig. 2 Magnetic field dependence of nonreciprocal resistivity  $\rho_{asym}^{2\omega}$  at 300K after the chirality control by the magnetic field sweep from the magnetic field *H*<sub>0</sub> (*H*<sub>0</sub>=±3T) with the application of electric current *j*<sub>0</sub>=0, ±8.0×10<sup>9</sup> A/m<sup>2</sup> [1].

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#### GIMRT International Co-Authored Paper

## CO<sub>2</sub>-Actuated Spin Transition Tuning in an Interdigitated Hofmann-Type Metal-Organic Framework

he tuning of the iron(II) spin transition temperature over a wide temperature range in cooperation with the gated CO<sub>2</sub> adsorption based on the varied CO<sub>2</sub> pressure was achieved in an interdigitated two-dimensional layered metal-organic framework, which is a novel case for developing CO<sub>2</sub>-responsive magnetic materials.

The increased anthropogenic emission level of CO<sub>2</sub> urges the development of CO<sub>2</sub>-responsive materials, but is it possible to regulate the inherent electronic properties through weak physisorption of a ubiquitous gas such as CO<sub>2</sub>? Herein, we intended to answer this imperative question by the first case of CO<sub>2</sub>-actuated variable spin-state stabilization in an interdigitated Hofmann-type metal-organic framework [Fe<sup>II</sup>Pd(CN)<sub>4</sub>L<sub>2</sub>] (**1**, L = methyl isonicotinate) [1].

Compound 1 did not adsorb N2 (77 K) and O2 (90 K). In contrast, a sharp transition appeared in the CO<sub>2</sub> adsorption isotherm and isobar (Fig. 1a), indicating adsorption. Magnetic gated measurements were conducted using a home-built gas cell under an external magnetic field of 1 kOe and varying CO<sub>2</sub> pressures (Fig. 1b), showing a wide shift in the transition temperature  $(T_{1/2})$  from 178 K at  $P_{CO2} = 0$  kPa to 229 K at  $P_{CO2} = 100$  kPa (defined by the average of cooling and heating). Interestingly, the emergence of a stepped behavior in the heating process below  $P_{CO2} = 10$  kPa and overlapping magnetic susceptibility values above  $P_{CO2} = 10$  kPa elucidate the selective low-spin state stabilization correlated with the extent of CO2 accommodation. Based on the magnetic response and phase transition diagrams obtained under the respective Pco2 conditions (Fig. 1c), a plausible scenario of spin-state switching can be interpreted as  $[\mathbf{1}(ls) + \mathbf{1}'(ls)] \rightarrow [\mathbf{1}(hs) + \mathbf{1}'(ls)] \rightarrow \mathbf{1}(hs)$  at  $P_{CO2} \leq$ 10 kPa, 1'(ls)  $\rightarrow$  1(hs) at 10 kPa <  $P_{CO2}$  < 32 kPa, and  $\mathbf{1}'(ls) \rightarrow \mathbf{1}'(hs) \rightarrow \mathbf{1}(hs)$  at  $P_{CO2} = 100$  kPa, where 1 and 1' represent the CO2-free and CO2accommodated states/moieties, respectively, and hs and Is represent the high-spin and low-spin states of Fe(II), respectively. Cooperative CO2 adsorption with spin transition based on the varied CO2 pressure corroborates a novel case for developing CO<sub>2</sub>-responsive magnetic materials.

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/ mol mol<sup>-1</sup> (a) 50 Amount 40 I 1.2 P<sub>CO2</sub> (kPa) 1.0 - 100 adsorbed / ml 0.8 Amount adsorbed / 32 30 10 0.6 3.2 20 0.4 10 STP) 0.2 0.0 0 ũ, 300 150 200 250 Temperature / K – 100 kPa –– 32 kPa –– 10 kPa (b)  $P_{\rm CO2}$ 3.2 kPa--- 1 kPa --- 0 kPa 4 K emu mol 3 160 200 240 160 200 240 T/K T/K (c) 260 T10(2) Heating sothern (1) Heating 240 Cooling Temperature / K 220 200 180 Solid-CC GC 160 0.1 10 100 Pressure / kPa

Fig. 1 (a) CO<sub>2</sub> adsorption isobar on the cooling process under several CO<sub>2</sub> pressures. (b)  $\chi T$ -T plots at 1000 Oe under CO<sub>2</sub> on cooling (left) and heating (right) processes. (c) *T*-P phase diagram to demonstrate the correlation of the gated-CO<sub>2</sub> adsorption and Fe(II) spin transition.

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#### International Co-Authored Paper

## High-Field Reentrant Superconductivity of Ultra-Clean Single Crystal UTe<sub>2</sub>

High-field magnetoresistivity measurements were performed on spin-triplet superconductor UTe<sub>2</sub> using the ultra-clean single crystals grown by the molten salt flux liquid transport (MSFLT) method. It is found that the field-reentrant superconductivity, which is detected initially only near  $H \parallel b$ -axis, extends up to the field angle,  $\theta$  tilted by 24 deg from *b* to *c*-axis. This reentrant superconductivity is further connected to the superconducting phase above the metamagnetic field ( $H_m > 40$  T for  $\theta > 24$  deg), revealing that the complex fluctuations are the driving force for this enigmatic superconductivity.

UTe2 is one of the most studied materials in condensed matter physics [1]. Superconductivity emerges below  $T_c = 1.6-2.1$ K in a paramagnetic ground state characterized by heavy electronic states. The most remarkable feature is that superconductivity remains robust against magnetic fields, surviving up to 35 T despite the relatively low Tc. Multiple superconducting phases are observed under both high pressure and high magnetic fields, strongly supporting a scenario of the spin-triplet state in UTe2. Field-induced (or reinforced) superconductivity is also known in ferromagnetic superconductors such as URhGe and UCoGe. Consequently, UTe2 was initially proposed to be an end member of the ferromagnetic superconductor family. However, experimental evidence indicates that the dominant magnetic fluctuations are antiferromagnetic, with an incommensurate wave vector, leaving the mechanism of superconductivity enigmatic.

To investigate the superconducting state in more detail, we conducted magnetoresistivity measurements on UTe<sub>2</sub> at high magnetic fields up to 36 T and low temperatures down to 50 mK, with varying field angles [2]. Ultra-clean single crystals

with a large residual resistivity ratio (RRR  $\approx$  500) were grown using the MSFLT method [3]. Figure 1 shows the full angular dependence of  $H_{c2}$  and  $H_m$  at low temperatures.  $H_{c2}$  is enhanced for  $H \parallel b$ -axis but is suppressed when the field is tilted from the *b*-axis towards the *a*-axis. In contrast, when tilted from the *b*-axis towards the *c*-axis, superconductivity persists over a wide range of field angles and is even reinforced above the metamagnetic field  $H_m$ , exceeding 40 T.

In URhGe, a ferromagnetic superconductor, the reentrant superconducting phase is linked to the

spin-reorientation field  $H_{\rm R}$ , which follows a 1/cos $\theta$  dependence due to Ising-type ferromagnetic fluctuations tuned by the field orientation. However, in UTe<sub>2</sub>, the field-reentrant superconductivity observed below and above  $H_{\rm m}$  near the "magic angle" ( $\theta \sim 24$  deg) cannot be explained by simple ferromagnetic fluctuations. Complex fluctuations involving antiferromagnetic, ferromagnetic, valence, and Fermi surface instabilities may contribute to this exotic superconducting state.

It is noteworthy that uranium compounds serve as an excellent platform for exploring exotic superconductivity and quantum phenomena in condensed matter physics, owing to the dual (itinerant/localized) nature of 5f electrons and strong spin-orbit coupling. Further discoveries of novel phenomena in these materials are highly anticipated.

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Fig. 1 Angular dependence of *H*<sub>c2</sub> and the metamagnetic field *H*<sub>m</sub> of highquality single crystals UTe<sub>2</sub> [2]. SC denotes superconductivity.

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## **Research Centers**

IMR KINKEN Research Highlights 2025



#### International Co-Authored Paper

### C-Axis Electrical Transport at the Metamagnetic Transition in the Heavy-Fermion Superconductor UTe<sub>2</sub> Under Pressure International Research Center for Nuclear Materials Science

he electrical resistivity of the unconventional superconductor UTe<sub>2</sub> exhibits significant anisotropy depending on the current direction in the normal state. We report that the resistivity peak  $\rho_c$  along the *c* axis at approximately 14.75 K aligns with the minimum in thermal expansion  $T^*$  along the *b* axis. Under a magnetic field along the *b* axis,  $T^*$  is traceable up to the metamagnetic transition at 6 K and 34.5 T, which corresponds to the critical point of the first order metamagnetic transition. Under pressure,  $T^*$  and  $H_m$  decrease until superconductivity vanishes, and antiferromagnetic order emerges. The phase diagrams at various pressures can be scaled by  $T^*$ , indicating its role in governing normal-state interactions.

The discovery of superconductivity in UTe<sub>2</sub> has raised an intense research effort due to the possible spin-triplet pairing. The strong enhancement of the superconducting upper critical field,  $H_{c2}$ , which exceeds by far the Pauli limit for all crystallographic axes, is a strong indication for this rare pairing state.

In this study, we investigated the field and pressure dependence of the different fluctuations by electrical resistivity measurements using the high quality single crystals UTe<sub>2</sub> [1].

Figure 1 shows the magnetoresistivity for the current along the a, b, and c axes under a magnetic field applied along the b axis. For J II a, the MSFgrown sample with Tsc = 2 K shows a similar field dependence to previous reports, with re-entrant superconductivity up to  $H_m$ . For J II b,  $\rho_0$  exhibits a large positive jump by a factor of 8.5 at  $H_{m}$ , much stronger than along the *a* axis. Interestingly, for J II c,  $\rho_{\rm C}$  decreases at H<sub>m</sub> by a factor of 1.45, in contrast to the increases along the *a* and *b* axes, and no strong anomaly is observed near Tsc. Above Tsc, the resistivity drop along c becomes more pronounced, resembling a crossover beyond the critical point of the metamagnetic transition. These anisotropic behaviors likely result from quasi-2D Fermi surfaces in UTe2. While conduction along a and b is dominated by cylindrical Fermi surfaces, conduction along c may be influenced by a heavy Z pocket detected in ARPES studies. However, recent dHvA measurements did not confirm a 3D pocket [2], suggesting further investigation is needed.

Under pressure,  $H_m$  and  $T^*$  decrease up to the critical pressure Pc. The phase diagram in the normal state below Pc scales with  $T^*$ , indicating the importance of this low-energy scale; the coherence along the *c*-axis governs the low temperature behavior.



Fig. 1 Magnetoresistivity of UTe2 for *H* II *b* at different temperatures with the current applied along *a*, *b*, and *c* axes. The inset in every panel gives the field range of the metamagnetic transition in an enlarged scale [1].

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#### GIMRT

## In-Situ Observations of Geometrically Necessary Dislocations and Fuel Debris in Nuclear Reactors

International Research Center for Nuclear Materials Science

hermal stability of geometrically necessary (GN) dislocations formed by Mn precipitates in A533B alloy was evaluated using in-situ weak-beam scanning transmission electron microscopy (WB-STEM) in nanoscale. In-situ X-ray absorption fine structure (XAFS) for a Zr/Y<sub>2</sub>O<sub>3</sub> mixture at extra-high temperature above 2000 K, successfully clarified the Zr oxidation and ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub> reaction from 1952 to 2519 K.

Dynamic electron/X-ray observations enable a deeper understanding of thermal relaxation and crystal growth processes. Here, we show the advanced in-situ studies about reactor pressure vessels [1] and fuel debris [2].

Figures 1 is in-situ WB-STEM imaging of GN dislocations at (a) 573 K, (b) 673 K, (c) 753 K, (d) 773 K, (e) 823 K, and (f) 873K, in the A533B RPV steel, which was provided by Chubu Electric Power Company (Hamaoka Nuclear Power Station, Japan) as part of the test piece, Hamaoka No. 1 reactor UT block (0.09 wt.%Cu). In isochronous annealing process imaging, the dynamic behavior of dislocations was successfully visualized using movie files with a spatial resolution of 0.4 nm/pixel and a temporal resolution of 1s/frame via WB-STEM. Results revealed thermal relaxation of local strain as high-density (above  $2.5 \times 10^{16}$  /m<sup>2</sup>) dislocations deformed into new subgrain boundaries via the GN dislocation network at control temperatures from 773K to 823 K.

Figures 2 shows the in-situ XAFS for a metal/ metal-oxide mixture at extra-high temperature above 2000 K has been desired in the field of nuclear safety engineering. In this study, we succeeded in simultaneous XAFS-XRD measurements of the Zr oxidation  $[Zr + O \rightarrow Zr(O) + ZrO_2]$  up to 1952 K and ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub> reaction from 1952 to 2519 K. The chemical shift during Zr oxidation was observed in the absorption spectra around the Zr K-edge, and the interatomic cation-cation and cation-oxygen distances obtained by the fitting analysis of EXAFS during the Y2O3-ZrO2 reaction are explained. Also, the temperature dependency of the anharmonic effect was investigated by comparing the fitted second- and third-order cumulants with the theoretical ones in which the Morse potential was applied as an interatomic potential, giving a good explanation about the local structure dvnamics.

Finally, in addition to in-situ observations, the Oarai Center provides essential research instruments



Fig. 1 In-situ WB-STEM of the GN dislocations formed by Mn precipitates in Hamaoka No. 1 reactor UT block (0.09 wt.%Cu) steel at control temperatures from 773K to 823 K [1].



Fig. 2 In-situ EXFS: Normalized absorption spectra at the Zr K-edge and (a) the dependency of E<sub>0</sub> on temperature [2].

such as ion beams fabrication of radioactive isotopes and nuclear fuel materials, fuel debris for users of the GIMRT program.

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## Anomalous Phase Transformation in Ti<sub>50-x</sub>Ni<sub>47+x</sub>Fe<sub>3</sub> Shape Memory Alloys

#### Cooperative Research and Development Center for Advanced Materials

Phase transformations among the parent (B2), intermediate (I), and rhombohedral (R) phases were investigated in Ti50-xNi47+xFe3 shape memory alloys. The B2/R transformation temperature and entropy change drastically decreased by the appearance of I phase transition. By in-situ TEM observation, it was confirmed that R phase had a fine cluster-like microstructure without twin boundaries even in the region where I phase transition actually existed. It can be said that the microstructure and phase stability of the R phase is strongly affected by the existence of the I phase.

Ti-Ni based alloys, known as shape memory alloys, are widely used for industrial and medical applications. The addition of a third element has been used to change the martensitic transformation behavior in Ti-Ni based alloys. Ti50Ni50-xFex alloys with  $1 \leq x \leq 3$  show a successive martensitic transformation from the B2 (Pm3m) to the B19'(P21/m) phase via the R (P3) phase. The temperatures of the B2/R transformations decrease monotonically with increasing Fe content and a broad endothermic peak due to a commensurateincommensurate (C-IC) transition appears in the heating curve of the specific heat measurement in which no B2/R phase transformation is detected [1]. The thermal and mechanical properties of B2/R and the C-IC transformations have mainly been investigated in ternary alloys with a composition fixed at 50 at.% Ti [1, 2]. The C-IC (denoted as B2/I hereafter) phase transformation affects not only the entropy change but also the transformation temperatures. However, the influences of the B2/I transition on the R phase transformation in Nirich region have been still unknown.

To elucidate the effect of I phase transition on the martensitic transformation behavior in Ti-Ni-Fe alloys, microstructures of Ti<sub>50-x</sub>Ni<sub>47+x</sub>Fe<sub>3</sub> (x = 0.00-1.00) were investigated [3]. The selected area diffraction pattern (SADP) taken from the [111]B2 incident beam direction at T = 87 K for the x = 0.00 alloy is shown in Fig. 1 (a). In Fig. 1 (b), the TEM specimen was tilted, so only 011-type reflections were excited. It is important to note that the n/3 011<sub>B2</sub> diffractions remain, which is in accordance with the fact that the x = 0.00 alloy shows R phase at this temperature. The dark-field image (DFI) at T = 87 K for the x = 0.00 exhibits a typical twin microstructure of the R phase as shown in Fig. 1(c). In the x = 0.35, the characteristic twin microstructure of the R phase is also observed at T = 87 K, but a cluster-like structure exists in the twin microstructure in Fig. 1(f). For the x = 0.40, the observation was performed at T = 87 and subsequently at 183 K, where the R phase and I phase,



Fig. 1 SADP taken from the  $[1\overline{1}1]_{B2}$  incident beam direction at 87 K for x = (a) 0.00, (d) 0.35, and (g) 0.40, and (j) at 183 K for x = 0.40. Two-beam patterns excited to 011B2 zone at 87 K for x = (b) 0.00, (e) 0.35, and (h) 0.40, and (k) at 183 K for x = 0.40. DFI taken from 1/3 011B2 spot at 87 K for x = (c) 0.00, (f) 0.35, and (i) 0.40, and (l) at 183 K for x = 0.40.

respectively, are expected to be detected in Fig. 1(g-i) and Fig. 1(j-i). It is worth noting that all the variants of the R phase were observed for x = 0.40, unlike those for the x = 0.00 and 0.35 alloys. This result means that the crystal structure of the sample changes from the R phase to the I phase during heating. By the similarity in the cluster-like structure between the I and R phases, it is deduced that the cluster regions in the I phase directly transform to the R phase, i.e., the I/R transition occurs in the only limited volume, but not the whole sample.

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#### GIMRT International Co-Authored Paper

### Progress of 33T Cryogen-Free Superconducting Magnet High Field Laboratory for Superconducting Materials

he 33T cryogen-free superconducting magnet (33T-CSM) project is underway at the HFLSM. In March 2024, the system without the HTS insert was installed and tested. The LTS outsert magnet consisting of three CuNb/Nb<sub>3</sub>Sn Rutherford cable coils and two NbTi Rutherford cable coils with an epoxy impregnation can generate 14 T in a 320 mm bore with 879 A. We have successfully cooled and tested the LTS coil without any problems. The 19 T-HTS insert was designed based on the robust REBCO coil technology we proposed. It will be installed in 2027.

A 33T cryogen-free superconducting magnet (33T-CSM) system excluding a high-temperature superconducting (HTS) insert was installed at HFLSM, IMR, Tohoku University in March 2024 (Fig. 1) [1]. The 33T-CSM consists of a \u00f668mm- 19 T REBCO (HTS) insert and a ¢320mm-14 T CuNb/ Nb<sub>3</sub>Sn and NbTi Rutherford (LTS) magnets. It has a 32 mm room temperature bore. An advanced high strength CuNb/ Nb<sub>3</sub>Sn Rutherford cables specially developed for the 33T-CSM with Furukawa Electric Co Ltd, enables a high-stress design with approximately 275 MPa in the Nb<sub>3</sub>Sn coil at 14 T. In addition, the Nb<sub>3</sub>Sn coils were fabricated by a reactand-wind (R&W) method combined with a repeated bending treatments (pre-bending treatments), which improves the critical current and the mechanical properties. The LTS magnets are cooled by one GM/JT cryocooler with 9 W of cooling capacity at 4.2K. The HTS magnet is cooled by four two-stage 4K-GM cryocoolers with 6 W of the cooling power in total at 4.2 K. Two single-stage cryocoolers are used for the radiation shields and high temperature ends of the HTS current leads.

The LTS magnets were cooled from room temperature to an operation temperature around 4.2 K for approximately 7.3 days. The test of the 14 T LTS magnet was successfully completed up to 839 A with the nominal maximum electromagnetic stress of 275 MPa after one training guench (Fig. 2). The design of the 19 T REBCO insert coil was also completed. It consists of 64 pancake coils with a "robust coil concept" we proposed. We demonstrated its efficiency and high performances with the large scale prototype coil. The maximum hoop strain estimated by FEM is about 0.3%, which is almost % less than irreversibility limit of REBCO tapes with 40 mm/side Cu stabilizer. The construction of the REBCO insert will be completed in 2027.



Fig. 1 33T-CSM installed at HFLSM



Fig. 2 Temperature profile of the LTS coil of 33T-CSM during operation [1].

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## Pressure-Tuned Quantum Criticality in the Large-D Antiferromagnet DTN

#### High Field Laboratory for Superconducting Materials

Employing high-frequency ESR in high pressure, we investigated that the pressure induced gap-full tomagnetic order type quantum phase transition in tetragonal easy-plane quantum antiferromagnet NiCl<sub>2</sub>·4SC(NH2)<sub>2</sub> (aka DTN). No lattice distortion was found in neutron diffraction at the phase transition and the high spin symmetry is preserved. Our study establishes that DTN is a perfect platform to investigate quantum critical phenomena in a system with *z*=1 critical exponent.

Magnetic insulators provide ideal models for studying quantum critical phenomena induced by the control of Hamiltonians by high magnetic field, high pressure, chemical doping and others. In magnetic field induced antiferromagnetic (AF) ordering, the excitation spectrum split by the Zeeman term. On the other hands, the high pressure can induce the spontaneous spin-symmetry break-down while keeping the degenerated spectrum. The pressureinduced transition belongs to another class of universality because of this nature. The key factor is the dynamic critical exponent z that links the characteristic energy of spin excitations to the momentum related to the critical state. Field-induced phase and the pressure-induced transitions are classified by z=2 and z=1, respectively. There difference originate from the nature of the excitation spectrum. In the latter, spectrum is linear, and it has mean-field critical exponents and the universal scaling of dynamic fluctuations with an amplitude mode.

Employing hydrostatic pressure in combination with high-field electron spin resonance (ESR) spectroscopy, ultrasound, a.c. susceptibility, and neutron-diffraction techniques. powder we demonstrate the possibility of driving the tetragonal easy-plane quantum antiferromagnet NiCl<sub>2</sub>·4SC(NH<sub>2</sub>)<sub>2</sub> (aka DTN) from the gapped disordered to a magnetically ordered phase. This transition is accompanied by the spin-gap closure at about 4.2 kbar and characterized by z=1 critical exponents, determined by the quasi-linear low-energy dispersion of spin excitations.

Selected ESR spectra of DTN taken at a frequency of 228 GHz at a temperature of 4 K at different pressures are shown in Fig. 1. Our experimental observations are supported by DMRG calculations, allowing us to quantitatively describe the pressuredriven evolution of critical fields and spin-Hamiltonian parameters in DTN.



Fig. 1 Pressure dependence of ESR spectrum at 228 GHz [1].



Fig. 2 Magnetic field-pressure phase diagram of DTN [1].

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### A New AB<sub>3</sub>-Based Alloy with Reversible Hydrogen Absorption and Desorption Reactions and Less Degradation Collaborative Research Center on Energy Materials

Hydrogen storage materials, which can store hydrogen as atomic states, have great advantages as compact hydrogen storage methods compared with gaseous and liquid hydrogen. By contrast, hydrogen storage capacities per total weight (gravimetric hydrogen densities), and cycling durability are demanded for practical applications. Herein, we show a new AB3-based alloy, Y0.68Mg0.32Co3.00, in which 1.68 mass% of hydrogen was stored. In addition, the gravimetric hydrogen density was maintained up to 100 cycles of hydrogen absorption and desorption reactions. Using X-ray and neutron diffraction, atomic arrangements during the hydrogen absorption reactions were also elucidated.

Intermetallic compounds AB<sub>x</sub> (A: Element in Group 1-5, B: element in Group 6-12 in the periodic table,  $0 < x \le 5$ ) store hydrogen atoms in interstitial sites in their lattices. Since AB<sub>x</sub> store hydrogen compacter than gaseous and liquid hydrogen, AB<sub>x</sub> is a promising hydrogen storage material. Although AB<sub>5</sub> (LaNi<sub>5</sub>-based alloy) has been industrially used as hydrogen storage materials, new materials with reversible hydrogen absorption and desorption reactions at moderate conditions, less degradation and higher hydrogen storage capacity have been demanded.

Recently, we have reported (Y, Mg)(Co, Ni)<sub>2</sub>, which was synthesized from YCo<sub>2</sub> and MgNi<sub>2</sub>, with reversible hydrogen absorption and desorption reactions [1]. Their hydrogen storage properties were depended on amounts of Mg and Co. To increase amounts of Co, YCo<sub>2</sub> and MgCo<sub>2</sub> were used as starting materials. Resulting that, (Y, Mg)Co<sub>3</sub> was yielded instead of (Y, Mg)Co<sub>2</sub>. The chemical composition could be Y0.68Mg0.32Co3.00, which stored 1.68 mass% of hydrogen and exhibited reversible hydrogen absorption and desorption reactions at 303 K. Interestingly, Y0.68Mg0.32Co3.00 showed less degradation up to 100 cycles of hydrogen absorption and desorption and desorption and desorption reactions at 303 K (Fig. 1) [2].

To understand the hydrogen absorption reactions viewed from atomic arrangements, we observed crystal structures by neutron diffraction under D<sub>2</sub> pressure. Based on the Rietveld refinements on the neutron diffraction data, D atom absorbed Y0.68Mg0.32Co3.00 was adopted a trigonal crystal structure with a = 5.27370(64) Å and c = 25.68827(553) Å. The crystal structure was composed of two kinds of polyhedra, which were capped hexagonal prism (orange in Fig, 1) and Laves polyhedron (green in Fig. 1). In the crystal structure (Fig. 1), D atoms located in



Fig. 1 (a) Hydrogen absorption reactions of Y0.68Mg0.32Co3.00 at 303 K and (b) crystal structure and local atomic arrangements of deuterium absorbed Y0.68Mg0.32C3.00.

inside of the polyhedra and in between those polyheda.

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GIMRT International Co-Authored Paper

## Contrasting Activity Profiles of Tin-Based Catalysts in Electrochemical CO<sub>2</sub> Reduction: pH-Responsive Differences Between Single-Atom and Polyatomic Configurations

Center for Computational Materials Science

By integrating data mining, ab initio computations, and modeling, we find single-atom Sn-N4-C and polyatomic Sn catalysts show opposite pH-dependent CO<sub>2</sub>RR volcano trends due to contrasting electric field responses of \*OCHO binding. We propose that distinct optimization strategies are needed for different Sn-based catalysts.

The pursuit of electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>RR) into valuable products like formic acid (HCOOH) has recently drawn considerable attention, particularly when integrated with renewable energy sources [1]. Tin (Sn)-based catalysts continue to captivate interest due to their noteworthy selectivity and activity toward HCOOH. Nevertheless, the underlying mechanisms governing pH-dependent performance variations between single-atom Sn-N4-C catalysts and polyatomic Sn species (e.g., SnO<sub>x</sub>, SnS<sub>x</sub>) remain insufficiently elucidated, hindering a comprehensive understanding of their catalytic behavior.

In this study, a comprehensive approach was employed to address this challenge. More than 2,000 experimental reports on CO<sub>2</sub>RR catalysts were analyzed through large-scale data mining, yielding an extensive dataset of Faradaic efficiencies and reaction conditions. Integrating these insights with density functional theory calculations, machine learning force field -accelerated molecular dynamics simulations, and pH-field coupled microkinetic modeling [2,3] allowed the us to systematically investigate the structural sensitivity and pH-dependent behavior of Sn-based catalysts, e.g. single-atom and polyatomic Sn catalysts.

The results revealed a striking contrast in how the key intermediate (\*OCHO) responds to electric fields. Specifically, the dipole moments of \*OCHO on singleatom Sn-N4-C and polyatomic Sn surfaces shift in opposite directions, leading to fundamentally different pH-dependent volcano trends (Fig. 1). Given the structural sensitivity of single-atom and polyatomic Sn-based catalysts, different optimized strategies are proposed. While increasing alkalinity enhances the activity of singleatom Sn-N4-C catalysts, polyatomic Sn catalysts require a different strategy: moderating the binding strength of \*OCHO to improve their performance. These theoretical insights were corroborated by experimental validations measuring turnover frequencies under neutral and alkaline conditions. The strong agreement between the predicted and observed results underscores the



0.67

0.50 0.75

Fig. 1 pH-sensitive modeling of CO<sub>2</sub>RR on Sn-N<sub>4</sub>-C single-atom catalysts (a) and polyatomic Sn (b). On the color bar, the right-hand side shows the correlation with the electric field, while the left-hand side indicates the link to pH. Lower electric field values align with more alkaline (basic) conditions, whereas higher fields correspond to acidic environments.

0.50 -0.25 0.00

robustness and accuracy of the proposed model.

In essence, this work provides new understanding of how structural differences in Sn-based catalysts influence their pH-dependent CO<sub>2</sub>RR performance. By elucidating the interplay between dipole-field interactions, adsorption energetics, and catalyst structure, the study offers practical guidance for designing Sn-based catalysts tailored to specific operating environments. This research not only supports the development of more efficient CO<sub>2</sub>RR electrocatalysts but also strengthens the conceptual framework needed to optimize reaction conditions. Ultimately, these findings can be extended to other *p*-block metal catalysts, guiding the future rational design of materials aimed at sustainable energy conversion.

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GIMRT

## Crystallization of *L*10, *L*12, and *D*022, Phases from the Parent Cr26.7Ni26.7Co26.7Si10B5P5 Amorphous Alloy

#### Quantum Beam Center for Materials Research

Chemically ordered face-centered cubic phases consisting mainly of Cr, Co, and Ni were synthesized by annealing a Cr<sub>26.7</sub>Ni<sub>26.7</sub>Co<sub>26.7</sub>Si<sub>10</sub>B<sub>5</sub>P<sub>5</sub> amorphous alloy (CrNiCo-MEA-am). The annealed Cr<sub>26.7</sub>Ni<sub>26.7</sub>Co<sub>26.7</sub>Si<sub>10</sub>B<sub>5</sub>P<sub>5</sub> sample was composed of Cr<sub>4.5</sub>BP<sub>2</sub>, Cr<sub>3</sub>Co<sub>5</sub>Si<sub>2</sub>, and fcc phases. Synchrotron radiation anomalous X-ray scattering (AXS) measurements confirmed that the annealed CrNiCo-MEA-am showed superlattice reflections from an *L*<sub>10</sub>- and/or *D*<sub>022</sub>-type ordered structure. The diffraction intensity of the superlattice reflection increased at the X-ray energy near the *K*-edge of Cr, suggesting that Cr is mainly ordered in the *L*<sub>10</sub>- and *D*<sub>022</sub>-type structures [1].

The amorphous phase obtained via liquid quenching does not transform into a crystalline phase at room temperature, however the crystallization process is readily prompted by the heating at a temperature of a few hundred kelvins. Recently, Makino et al. [2] reported that the FeNi L10 phase with a chemical ordering of Fe and Ni, could be obtained by annealing amorphous Fe42Ni41.3Si8B4P4Cu0.7 alloy for several days. The locally ordered amorphous structure and fast diffusion during the crystallization are considered to be the reasons for the precipitation of this interesting FeNi L10 structures. Here, we studied the crystallization process of amorphous alloy with equimolar amounts of CrNiCo-MEA. We evaluated the chemical ordering developed in a crystallized fcc solid solution through anomalous X-ray scattering (AXS) and scanning transition electron microscopy (STEM) observations. It may be added that theoretical approaches suggests the formation of a chemical short-range ordered (SRO) structure in the parent CrNiCo-MEA.

An alloy ingot with a nominal composition of Cr26.7Ni26.7Co26.7Si10B5P5 was prepared using a conventional highfrequency induction furnace. CrNiCo-MEA-am ribbon samples approximately 20 µm thick and 2 mm wide were produced via a single-roller melt-spinning technique in an Ar atmosphere. Laboratory X-ray diffraction (XRD) measurements using Mo K $\alpha$ radiation confirmed that the prepared ribbon-shaped samples were an amorphous single phase. The crystallization temperature  $T_x$  of CrNiCo-MEA-am was defined as 770 K from the first exothermic peak measured via differential scanning calorimetry (DSC) with a heating rate of 40 K/min. Chemically ordered crystalline phases were obtained by heating amorphous metals in an electric furnace under an Ar-2 vol%H2 gas flow. AXS-XRD measurements were performed at a synchrotron radiation facility at the BL7C beamline stations of the Institute of Materials Structure Science (IMSS), Tsukuba, Japan. A pair of incident energies, which were 25 and 300 eV below the Cr, Co, and Ni K-absorption edges, was used in the AXS measurements.

Figure 1 shows the enlarged XRD profile measured at the energies of the Cr, Co, and Ni *K*-edge, where 001 superlattice reflections of *L*<sub>10</sub> and/or *L*<sub>12</sub>, 002 and 101 superlattice reflections of *D*<sub>022</sub> are observed. The superlattice reflections at Q = 17.7 and 20.4 nm<sup>-1</sup> for *L*<sub>10</sub> and/or *L*<sub>12</sub> and *D*<sub>022</sub>, exhibit significant intensity



Fig. 1 AXS-XRD at the K- absorption edges of Cr, Co, and Ni.



Fig. 2 Reconstructed (a) DF- and (b) BF-STEM images and an NBED pattern (c) taken from a region enclosed by squares in (a, b) on the basis of the 4D-STEM dataset.

differences at the Cr *K*-edge. These results readily suggest that Cr is significantly involved in the chemical ordering of these *L*10, *L*12, and *D*022 phases. The structural models of *L*10, *L*12, and *D*022-typed structures with the chemical ordering of Cr and Co0.5Ni0.5 were tested. The model calculation well reproduced the observed diffraction intensities for the superlattice reflections. The virtual DF-STEM image reconstructed using a spot region corresponding to the superlattice 110 reflection is also shown in Fig. 2. The size of the grains exhibiting superlattice reflections was confirmed to be approximately 20 nm, and further STEM–EDS analysis of the fcc-based superstructure phases indicated a high Cr concentration (Cr70 at%), which was consistent with the trend of the proposed *L*10 (Cr50 at%) and *L*12 (Cr75 at%)-type structure.

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#### International Co-Authored Paper

## Influence of Chemical Composition on the Functional Properties of Ni50Mn50-xSbx Metamagnetic Shape Memory Alloys

#### International Collaboration Center (ICC-IMR)

Sb addition to AFM Ni50Mn50 alloy induces FM interaction and lowers Néel temperature. Dependence of Néel temperature on Sb content was computed for Ni50Mn50-xSbx alloys. Temperature-composition phase diagram of Ni50Mn50-xSbx system was constructed. Competing AFM and FM interactions lead to a spin glass state. Magnetic ordering significantly affects low-temperature specific heat and electronic coefficient.

Ni-Mn-based magnetic shape memory alloys possess distinctive properties such as the magnetocaloric effect, elastocaloric effect, shape memory effect, superelasticity, and giant magnetoresistance, making them highly promising for various applications. Among these, the Ni-Mn-Z (Z = In, Sn, Sb) system is notable for its rich phase diagram and the possibility to tailor its functional properties through alloying with Z elements. In particular, in Ni50Mn50xZx alloys, the martensitic transformation (MT) occurs at lower Z concentrations, whereas higher Z concentrations keep the alloy in a parent ferromagnetic (FM) austenitic phase [1]. The low-temperature martensitic phase of Ni50Mn50-xZx alloys remains a topic of ongoing research.

In this work, we have conducted a comprehensive study on Ni50Mn50-xSbx alloys [2]. Through a combination of

magnetization experiments, differential scanning calorimetry, low-temperature specific heat measurements, along with its theoretical analysis, we have elucidated the intricate magnetic and electronic properties of this alloy system. Our primary objective has been to unravel the fundamental aspects of magnetic transitions within the Ni-Mn-Sb alloy system. Additionally, we have constructed a temperature-concentration phase diagram for Ni-Mn-Sb alloys, thereby contributing to a more thorough understanding of its phase behavior.

The altering Sb content in Ni50Mn50-xSbx alloys induces variations in magnetic interactions and phase transitions. The addition of Sb to Ni50Mn50, which is collinear antiferromagnet (AFM) with a high Néel temperature, induces ferromagnetic interaction and leads to the decrease of Néel temperature. The compositional dependence of Néel temperature was computed from magnetic data. Increasing Sb content reduces characteristic temperatures for AFM interaction and elevates characteristic



Fig. 1 The AFM (blue region) and FM (red region) interactions in Ni50Mn50xSbx system giving rise to spin glass state (pink region). Characteristic temperatures of AFM interaction: computed (black circles) and estimated from experiments (open circles).

temperatures for FM interaction. Figure 1 displays the characteristic temperature of AFM (blue region) and FM (red region) interaction in Ni50Mn50-xSbx system. The overlap of these regions gives rise to a spin glass state [2]. The blue line corresponds to MT transition temperature. We identified six distinct magnetic phases in the Ni50Mn50-xSbx system depending on temperature and Sb concentration as shown in Fig. 1. It includes: antiferromagnetic martensite (AFM M), paramagnetic martensite (PM M), ferromagnetic martensite (FM M), spin glass or blocking state (SG or BS) within the martensitic state, and paramagnetic austenite (PM A) and ferromagnetic austenite (FM A) within the austenitic state.

The experimental investigation of lowtemperature specific heat of metallic alloys is of considerable significance due to its close connection to the underlying electronic properties. Indeed, the analysis of measurements of low-temperature specific heat is commonly used for the empirical estimation of electronic specific heat coefficient  $\gamma$ and Debye temperature *T*<sub>D</sub>. However, in the case of consideration of magnetic solid the influence of the magnetic ordering should be accurately accounted for the proper estimation of the electronic, lattice, and magnetic contributions to the specific heat [3]. Understanding specific heat behavior in relation to magnetic ordering is crucial for characterizing the thermodynamic and electronic properties of magnetic materials. This influence is especially pronounced for metamagnetic Ni-Mn-Z (Z = In, Sn, Sb) alloys, where the drastic changes in the magnetic characteristics occur depending on Z concentration.

In present work it has been shown that lowtemperature specific heat measured for Ni<sub>50</sub>Mn<sub>50-</sub> *x*Sb*x* alloys with  $x \ge 17$  being in the FM parent state is significantly different from that measured for the alloys, with  $x \le 16$ , being in martensitic phase with weak magnetism. Through a detailed experimental analysis and theoretical considerations, we aim to accurately estimate the electronic, magnetic and lattice contributions to low-temperature specific heat and explore the dependence of the  $\gamma$  and  $T_D$  on Sb content in both parent and martensite phases [2].

The procedure for the evaluation of the magnetic part of the specific heat of FM solid was elaborated in [3]. The application of this procedure to different Ni50Mn50-xSbx alloys resulted in the concentration

dependence of electronic specific heat coefficient and Debye temperature shown in Fig. 2. For the FM austenite region, the filled circles represent the electronic specific heat coefficient and Debye temperature calculated with the account of the magnetic contribution to specific heat (non-linear fit), while open circles denote results from the linear fit, which excludes the magnetic system's contribution. It is seen that disregard of the magnetic contribution in this phase results in an overestimation of the electronic coefficient by a factor of 2 and noticeable underestimation the Debye of temperature.

Importantly, the described behavior may extend to other Ni50Mn50-xZx (Z = In, Sn) alloys, where the addition of Z elements leads to the introduction of ferromagnetic interaction.

The results of this collaborative study were published in [2], and support from ICC-IMR was acknowledged.

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Fig. 2 Evaluated electronic specific heat coefficient  $\gamma$  and Debye temperature  $T_D$  of NisoMnso-xSbx alloys as a function of concentration x. The filled circles show  $\gamma$  and  $T_D$  estimated with the account of magnetic contribution to the specific heat (non-linear fit), while the open circles correspond to the linear fit, which disregards the contribution of magnetic system. Lines are guides for eyes.

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## Metallization of the Mott Insulator Ca<sub>2</sub>RuO<sub>4</sub> by Ion-Gating

Laboratory of Low Temperature Materials Science

he Mott insulator Ca<sub>2</sub>RuO<sub>4</sub> is known to transfer into a metal by applying a voltage accompanied by a large bias current. We have achieved this metallization without the effect of current flow by using an ionic gating to the single crystal surface. The reduction in resistance of up to 97% suggests that the surface gating induces a bulk-like structural change.

The Mott insulator Ca2RuO4 (CRO) has the unique property of switching into to a metal by applying an electric field of ~40 V/cm at 295 K through the nonlinear dynamical process [1]. This electric-filed induced insulator-metal transition is attractive from the viewpoint of not only fundamental physics but also application toward the Mott device. However, there remains debate as to whether the switching occurs by applying an electric field alone, independent of Joule heating effects caused by the current flow, which sometimes prevents us to know the intrinsic phenomena. Therefore, the observation of metallization using an electrostatic method has been desired.

To tackle this issue, we prepared electric doublelayer transistor (EDLT) devices, as shown in Fig. 1(a), using CRO single crystals with the freshly cleaved (001) surfaces (0.05-0.1 mm thick) [2]. We found a resistance drop by applying the positive gate voltage  $V_{G}$  above 3 V, corresponding to electron doping, at 260 K. The reversibility of the gating process, implying electrostatic behavior, was also checked between  $V_{G} = 0$  V and 4 V. A distinctive feature of the CRO-EDLT device is its aging effect showing long-term resistance decrease over several months at fixed VG. Figure 1(b) shows temperature dependence of resistance R(T) as a function V<sub>G</sub> and waiting time t (days) after applying  $V_{\rm G}$  at 260 K. The resistance at 260 K, initially 700  $\Omega$  (V<sub>G</sub> < 3 V), continues to decrease over time, reaching 18  $\Omega$  (V<sub>G</sub> =4 V) after 285 days, which correspond to ~97% reduction of resistance. Along with this decrease, R(T) also changes from the activation type to almost temperature-independent behavior with  $dR/dT \sim -0.35 \Omega/K$ , implying the successful metallization of CRO without the Joule heating effect.

The ion-gated metallization in CRO, characterized by long-term progression, is quite rare and hard to explain in terms of a conventional electrostatic carrier doping at the surface, which is a well-known function of EDLT. Indeed, the estimated depth of metallization is ~100 nm, which is much larger than the value expected for surface doping only. From the fact that CRO is sensitive to structural changes in metallization through the strong electron–lattice coupling, it is suggested that



Fig. 1 (a) A schematic cross-section drawing and top-view photo of a CRO-EDLT device. (b) R(T) curves measured as a function  $V_{G}$  and waiting time t (days) after applying  $V_{G}$  at 260 K.

the enormous resistance reduction in this study is most likely due to the bulk-like structural change extending into the crystal interior, which is triggered by initial surface metallization by gating.

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## **Research Facility for Physics and Chemistry of Radioactive and Nuclear Materials**

#### Laboratory of Alpha-Ray Emitters

More than 190 species of radioisotopes and nuclear materials are available for study at the Laboratory of Alpha-Ray Emitters. This laboratory is one of the most important centers worldwide for studying the physical and chemical properties of radioactive materials such as actinide compounds. Researchers from many leading universities and institutes all over Japan visit this facility every year to prepare a variety of materials and conduct chemical and physical experiments.

The Laboratory of Alpha-Ray Emitters provides a research environment for the study of 190 radionuclides and elements, especially alpha-ray emitters, such as actinide. This lab functions as a source for the preparation of pure crystals of actinide compounds, providing them to other universities and to synchrotron particle accelerators. In the past decade, actinium-225 (Ac-225), one of the actinides, has been provided as an inter-university collaboration to other universities and research centers. The radiation-controlled area of this laboratory includes three chemical rooms, three physical rooms and other facilities that are equipped with local exhaust ventilation systems, making the handling of various kinds of radioactive material possible. Many spectrometers, including those for gamma rays and alpha rays, are available.

A nuclear clock is a next-generation frequency standard candidate based on the resonance frequency of nuclear transitions. Nuclear transitions are much less susceptible to fluctuations in external electromagnetic fields than electronic transitions used in existing atomic clocks. As a result, the nuclear clock is expected to achieve frequency accuracy exceeding the existing clocks. Thorium-229 has attracted attention as an isotope that can realize nuclear clocks. This is because thorium-229 has a nuclear-excited state ("isomer") with an energy of only 8.4 eV, which can be excited by a laser. The resonance frequency of the nuclear transition between the ground state and the isomer of thorium-229 can be determined by high-precision direct laser spectroscopy of nuclei. One of the platforms to realize a nuclear clock is an ion trap. Towards a trapped-ion nuclear clock, we developed a method to trap thorium-229 ions in the nuclear ground state and isomer and a laser spectroscopy technique to selectively detect thorium-229 ions depending on their nuclear states. Using the thorium-229 isomer ions in a trap, we measured the

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Figure: The signal from thorium-229 isomer ions was extracted (green) as a difference between signals from ions in the isomer and nuclear ground state (red) and those from the nuclear ground state only (blue).

isomer lifetime, which was an essential parameter for the realization of nuclear clocks [1]. The sensitivity of the thorium-229 nuclear clock to variations in the fine structure constant is predicted to be approximately 1000 times larger than that of existing atomic clocks. Therefore, a nuclear clock is also expected to be a highly sensitive quantum sensor for fundamental physics research such as test of constancy of fundamental constants. Our achievement established a foundation for nuclear clocks based on trapped ions and their future applications.

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### Three-Dimensional Characterization for Advanced Materials Using Focused Ion Beam with Serial Sectioning Technology Analytical Research Core for Advanced Materials

he Analytical Research Core for Advanced Materials serves as an infrastructure for researchers not only in IMR but also outside the university by offering various elemental analytical methods and up-to-date structural characterization techniques, including aberration corrected microscopy, which makes possible atomic resolution observation as well as three-dimensional examination of a wide range of materials.

The Analytical Research Core for Advanced Materials (ARCAM) gives not only elemental composition data, and supports Transmission electron microscopy (TEM) analysis of metal and inorganic materials, but also offers various machining capability by using Focused Ion Beam (FIB) apparatus. We also develop analytical procedures in order to obtain reliable analytical data. The ARCAM assays major and trace elements in consigned samples by using the following methods: ICP-AES, ICP-MS, flame and graphite furnace AAS, microwave induced plasma AES, CS/ON/H analysis, XRF, ion chromatography, and conventional chemical analyses including gravimetric analysis, titrimetric analysis and spectrophotometry. Additionally, we provide TEM analysis services (which enable evaluation of microstructures, crystal structures and chemical compositions in nano-/meso- scale) on structural and functional materials and microdevices.

ARCAM is also heavily involved in the userfacility network, which has been supported by the government. Namely, so-called nanotechnology platform (up to 2021fy), and advanced research infrastructure for materials and nanotechnology in Japan (ARIM, 2021fy onward), both supported by MEXT. Researchers in academia and industries have access to our facility under these programs, and one can request technical as well as scientific support to us via CINTS (Center for integrated Nanotechnology Support, Tohoku Universitv). Facilities that ARCAM provides via ARIM include focused-ion beam apparatus and aberration corrected microscope, both of which are currently heavily used by researchers in Japan and overseas.

For instance, to correlate the catalytic behaviors of an alloy system with their microstructure, microscale three-dimensional evaluation of the material is necessary, since it is often their surface morphology and chemistry, which govern the final performance.



Fig.1 FIB equipped with Ga-ion beam column and field emission SEM. This apparatus is open for users outside campus.

To that end, we provide FIB characterization technique based on three-dimensional serial sectioning. Recent application include a study on porous Ni-Pt alloy, which gives superior hydrogen evolution, carried out by professor Fukumoto's group in Akita University. In the study, the internal structure obtained by serial sectioning was compared with that by X-ray tomography [1].

We also offer our aberration corrected TEM for a wide range of researchers nation-wide. For example, Professor Suemasu's group in Tsukuba university recently clarified the antiferromagnetic coupling in ferrimagnetic Mn4N-based bilayer structures. Here, the microscope was employed to reveal the interfacial structure at the atomic level, thereby relating the arrangement of atoms with magnetic coupling phenomenon [2].

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## Launching a Transformative Interdisciplinary Research Initiative at the Institute for Materials Research (IMR) at Tohoku University in Japan: Innovative Knowledge Hub for Humanities and Materials Science (IKH)

Innovative Knowledge Hub for Humanities and Materials Science

ohoku University's IMR launched an interdisciplinary initiative, Innovative Knowledge Hub (IKH), integrating materials science and humanities in September 2023. Funded by the Ministry of Education, it links institutes with different backgrounds. GIMRT opened a new IKH research area in 2024, receiving 10 proposals. Projects like crystal sculptures and monthly online forums highlight its innovative approach.

Tohoku University's Institute for Materials Research (IMR) launched the Innovative Knowledge Hub for Humanities and Materials Science (IKH) project in September 2023, supported by the Ministry of Education, Culture, Sports, Science, and Technology. This initiative, part of the "Programs for the Formation of Interdisciplinary Research Hubs," promotes collaboration between various research centers (https://ikh.imr. tohoku.ac.jp). Research Institute for the Dynamics of Civilization, Okayama University signed an Agreement on the Promotion of an Interdisciplinary Hub for IKH [1]. In April 2024, a liaison office was set up to broaden research collaborations, engaging seven other institutions nationwide. One primary focus is cultural heritage studies, where materials science techniques, such as neutron beams and synchrotron radiation, are used for nondestructive analysis of artifacts, offering insights into the construction of cultures and societies.

In 2024, IMR's Global Institute for Materials Research Tohoku (GIMRT) introduced a new research area within IKH, encouraging projects that merge materials science and humanities. In December, 10 projects were submitted, with applicants receiving guidance to refine their methodologies. A notable collaboration with Joshibi University of Art and Design in 2023 resulted in a sculpture, *Connotation and Extension of Time*, created using metal crystals. This work exhibited at JOSHIBI METAL WORKS 2024, sparked further academic research, including a doctoral thesis on crystal structures. Crystals have great potential to connect materials science with the humanities, making crystal sculptures a valuable educational resource. The sculpture was also displayed at IMR [2], drawing interest from secondary school students considering careers in art, humanities, science, and technology.

IKH also launched monthly online research meetings called units, which initially focused on metal artifacts. These sessions bring together archaeologists from diverse regions to share experiences, discuss challenges, and learn about advanced techniques such as X-ray CT, EDS, EMPA, Raman, and neutron diffraction. IKH's initiative showcases the transformative potential of integrating materials science with the



Fig. 1 Participating institutions and organizations in Japan's Innovative Knowledge Hub for Humanities and Materials Science (IKH). The new program promotes networking between different academic fields, focusing on the humanities and materials science.



Fig. 2 (Left) Dr. A. Fujisawa gave a talk for the IKH's first "Unit" session on metal artifacts, with its X-ray CT demonstration by Dr. H. Kano, broadcast online from the Center for Academic Resources and Archives. (Right) The image obtained in advance by X-ray CT.

humanities, and its future developments are highly anticipated.

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