

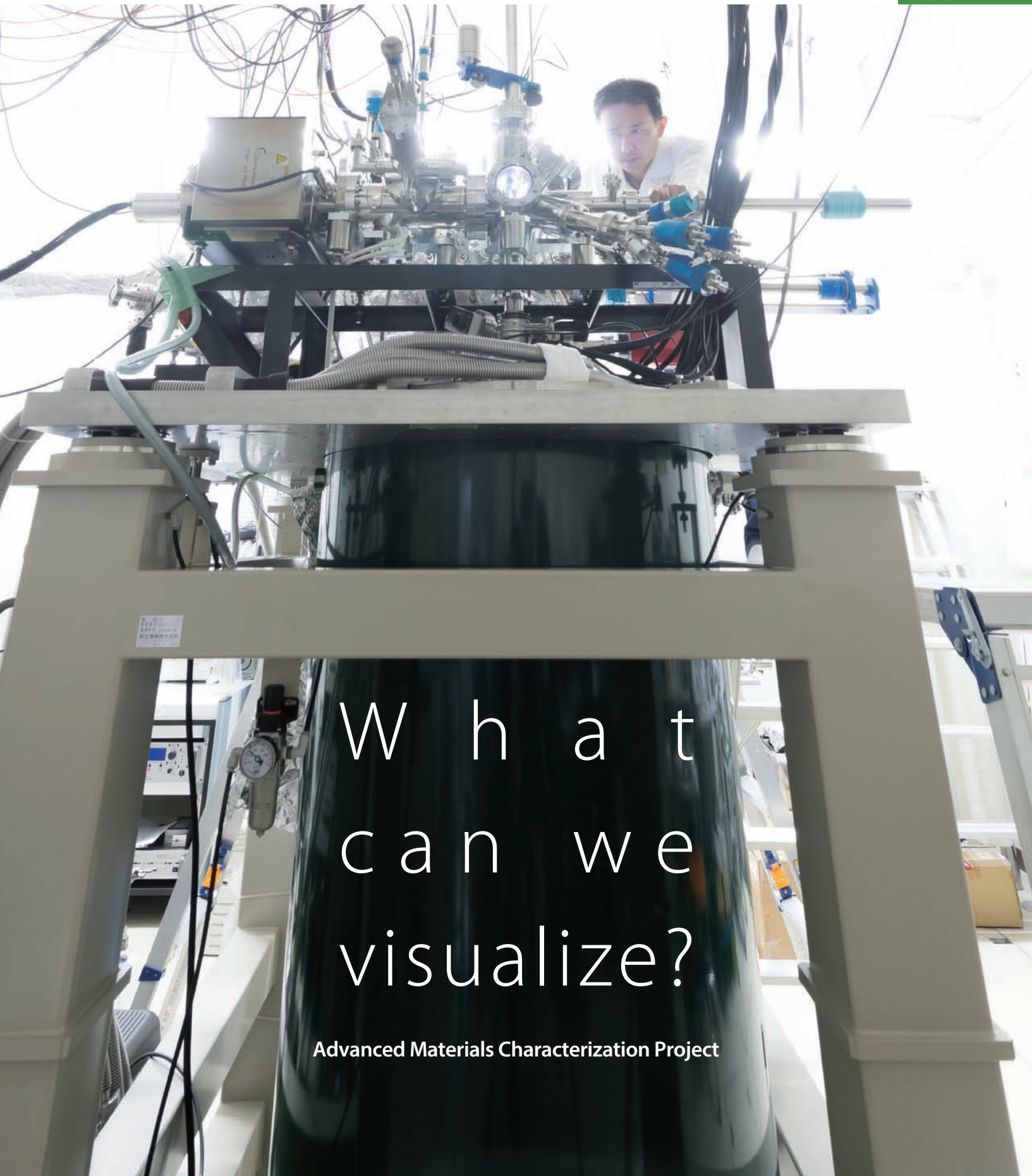
NIMS NOW

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W h a t
c a n w e
v i s u a l i z e ?

Advanced Materials Characterization Project

What can we visualize?

Advanced Materials Characterization Project

A super-resolution electron microscope has made it possible to accurately examine even atomic arrangements. This is a critical technological advancement in terms of moving basic research forward.

Material researchers are ambitious—they seek to observe and measure various materials more accurately, in finer detail, and under special conditions. They want to know about the structure and properties of new materials. These ambitions drive the advancement of characterization technologies and there is no end to this evolution. New characterization technologies allow material researchers to step into unknown territories of materials science.

Material researchers endeavor to visualize details with accuracy and visualize things which no one has seen before. NIMS's project for the development of advanced materials characterization technologies provides cutting-edge measurement and analysis technologies that enable material researchers to carry out advanced material studies.





Advanced Characterization Technologies for Realization of Unknown Properties: Key Technologies that Facilitate Innovation

Division Director, Advanced Key Technologies
Unit Director, Nano Characterization Unit
Daisuke Fujita

Significance of advanced characterization technologies to characterize materials: Plan-Do-See cycle

Based on NIMS's third mid-term plan (2011-2015), we, the research team in the Advanced Key Technologies Division, are currently working on the "development and application of advanced characterization technologies," which is one of five projects assigned to our division.

The Advanced Key Technologies Division carries out research and development of advanced core technologies which are often needed for various material studies performed across the NIMS organization. Such technologies include those that allow comprehensive characterization of materials from the surface to inside (the "See" step of the cycle), simulation technologies for analyzing physical properties of materials and for estimating and designing purposes (the "Plan" step of the cycle), and synthesizing, nano-fabrication and processing technologies for producing materials from basic structural units (e.g., particles and organic molecules) (the "Do" step of the cycle).

We are aiming to develop a common platform that will facilitate efficient material studies by using the framework of the Plan-Do-See cycle and by creating a feedback circuit that will encourage collaboration between researchers (Fig. 1).

The "See" part of the Plan-Do-See cycle, represented by measurement technologies, plays a vital role in material studies. For example, the development of a super-resolution electron microscope enabled accurate observation of the atomic arrangement structure in materials, which was nearly impossible before. The acquisition of such structural information has allowed

computational scientists to estimate electronic states and functional properties of a given material.

In addition, nano-scale observation and measurement of various structures and properties of new materials in an actual operation environment (i.e., active nano-characterization) allow material researchers to create and optimize new nano-processing technology^[1]. Some researchers believe that advanced measurement and analysis technologies will lead to new discoveries^[2]. And these technologies literally demonstrate the saying, "Seeing is believing." Furthermore, since these technologies lead to the creation of new materials, we would also add that these technologies demonstrate, "Seeing is creating."

Mission and concept behind NIMS's advanced characterization technologies

The mission of NIMS's project for the development and application of advanced material characterization technologies is to develop such technologies that will meet the social needs and to use them for the creation of novel materials. We provide support for NIMS to maintain its competitiveness and capacity to carry out basic research for the development of environment and energy materials as well as next-generation information communication materials which have high social demand. Novel functions of new materials are attributed to the structure, composition, arrangement, and electron and spin states in surfaces, interfaces and bulk materials. Based on this view, scientists are attempting to understand the basic mechanisms behind the novel functions at an atomic level and in multiple-scale

studies. In order to meet the social demand and expectations, it is vital for us to develop a platform that will support world-class and comprehensive studies on advanced material characterization and provide it to interested researchers. To prepare such platform, we will need to combine material evaluation methods such as surface sensitivity and bulk sensitivity studies, assessments of single crystallinity and amorphousness, and nanoscale and macroscale studies.

From this viewpoint, NIMS's advanced characterization project team set up the following six subthemes based on the key concepts of comprehensiveness and complementarity.

(1) Development and application of advanced technologies for the characterization of surface sensitivity

(Daisuke Fujita, Nano Characterization Unit, Surface Characterization Group)

(2) Development and application of advanced technologies for surface analysis

(Shigeo Tanuma, Nano Characterization Unit, Surface Chemical Analysis Group)

(3) Development and application of cutting-edge electron microscopy technology

(Koji Kimoto, Surface Physics and Structure Unit, Electron Microscopy Group)

(4) Development and application of characterization technology for high field nuclear magnetic resonance (NMR)

(Tadashi Shimizu, Nano Characterization Unit, High Field NMR Group)

(5) Development and application of characterization technology for strong neutron beams

(Hideaki Kitazawa, Quantum Beam Unit, Neutron Scattering Group)

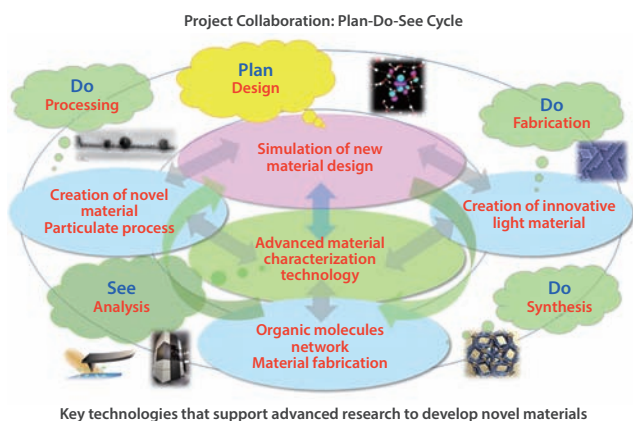


Fig. 1 Collaborative work in the framework of the Plan-Do-See cycle conceptualized in the mid-term project plan by the Advanced Key Technologies Division.

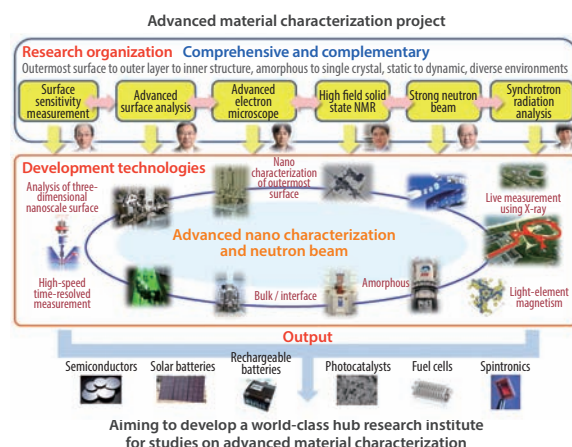


Fig. 2 Organization and objectives regarding the development and application of advanced material characterization technologies in NIMS's mid-term plan.

(6) Development and application of advanced characterization technology using synchrotron radiation

(Kenji Sakurai, Quantum Beam Unit, X-Ray Physics Group)

We are aiming to support the development and application of advanced characterization technologies that will meet diverse needs of society and to develop a world-class hub research center (Fig. 2).

Advanced measurement technologies that accelerate innovation

The importance of innovative characterization technologies is well recognized in industrialized western countries. For example, the National Institute of Standards and Technology (NIST), in the United States, concluded that the advancement of characterization technologies is vital based on its comprehensive study on the measurement systems present in the U.S., and presented some specific cases illustrating that slow advancement in characterization technologies is a barrier to innovative work in diverse industrial fields^[3]. According to a survey by the National Institute of Advanced Industrial Science and Technology concerning the global competitiveness of analytical instrument industries, Japan is in second place in terms of global market share (14%) after the United States (66%). However, Germany, which is currently in third place with 13% share, is rapidly catching up with Japan^[4]. In both the U.S. and Germany, their national governments are leading the development of advanced characterization instruments and are also promoting the wide use of such technologies.

Similarly, we as an incorporated administrative research institute should lead the high-risk development of advanced characterization technologies. Based on this perspective, NIMS's ad-

vanced material characterization project team is developing world-class technologies for core competence in line with the subthemes listed above. Some of the examples are shown in Fig. 3.

We are developing world-class measurement technologies such as a multiple-extreme condition scanning tunneling microscope, an electron microscope capable of analyzing a single atom with 50-picometer spatial resolution, high field solid state NMR, and a de facto standard system that allows three-dimensional visualization of crystals and electron structures.

Promotion of sharing, standardization and further contribution to society

We as innovators of characterization technologies are aiming to create a platform which will facilitate the wide use of such technologies we have developed. By making these measurement instruments available for shared use by researchers, engineers and students regardless of their affiliation, we hope to facilitate more innovations, encourage the development and wider use of such instruments, and provide training to prospective researchers. Many of our team members taking part in NIMS's advanced material characterization project are also participating in the microstructural analysis platform project sponsored by the Ministry of Education, Culture, Sports, Science and Technology, making use of our advanced nanomaterial characterization facilities. By doing so, they are making our advanced characterization facilities available to researchers across Japan. Furthermore, in order to promote the global use of those technologies, we are promoting international standardization which is vital to facilitate collaborative research by working with such organizations as the International Organization for Standardization (ISO)¹⁾ and the Versailles Project on Advanced Materials and Stan-

dards (VAMAS)²⁾.

We are also taking initiatives to meet the needs of local communities. We have been publicizing air radiation dose information measured at three different NIMS properties in Tsukuba City since 2011. In addition, by holding open seminars, we are striving to provide accurate information on radiation measurements and decontamination, which local communities and local government staff are particularly interested in. Furthermore, to widely communicate our research results and train prospective researchers, we hold symposiums and international meetings on advanced characterization technologies in cooperation with researchers both in Japan and overseas (Fig. 4).

As we described above, we have been developing a hub research center for studies on advanced material characterization technologies with our mission being to prepare a common research platform, work on international standardization, contribute to society, and train prospective researchers, in addition to our fundamental mission to develop advanced characterization technologies. We would like to use our facilities for diverse purposes.

- [1] Fujita, D. 2002. Intellectual platform for active nano-characterization. *Materia Japan*. 41: 623-627.
- [2] Nihei, Y. 2011. Characterization analysis technologies facilitate revealing new properties. *NIMS Now*. 11 (1).
- [3] National Institute of Standards and Technology (NIST). 2007. An Assessment of the United States Measurement System: Addressing Measurement Barriers to Accelerate Innovation. NIST Special Publication 1048.
- [4] National Institute of Advanced Industrial Science and Technology (AIST). 2011. Strengthening Japanese analytical instrument industries in global competition. AIST study report.

- 1) ISO (International Organization for Standardization): a non-governmental organization that sets up international standards for industries.
- 2) VAMAS (Versailles Project on Advanced Materials and Standards): an international joint research scheme for pre-standardization.

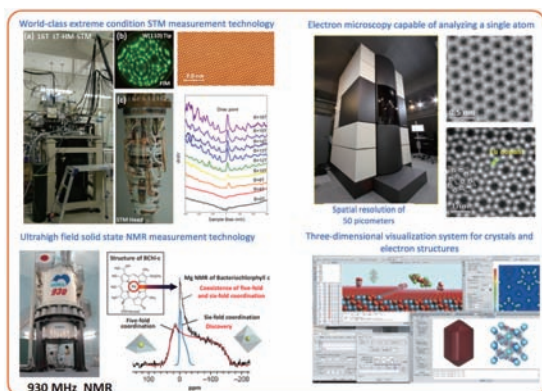


Fig. 3 Examples of world-class technologies for core competence that were developed during the advanced material characterization project.

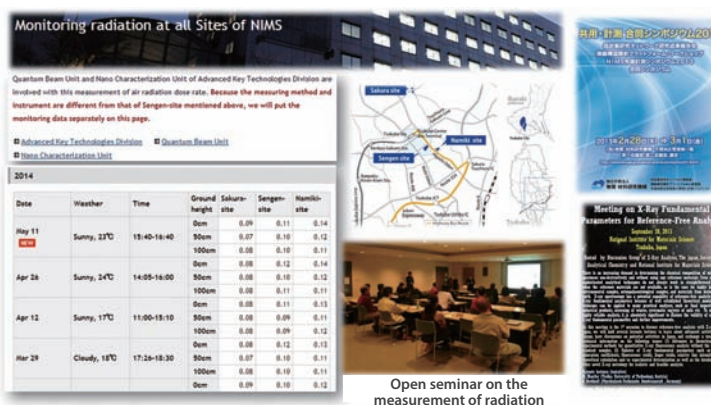


Fig. 4 Our initiatives to meet social needs: regular publication of air radiation doses measured in three NIMS properties in Tsukuba City; holding of open seminars on the measurement of radiation; and holding of symposiums and international meetings on advanced characterization technologies.

Profile

Daisuke Fujita Doctor of Engineering. After completing a master's program at the School of Engineering, the University of Tokyo, in 1986, worked as a research associate at the Institute of Industrial Science, the University of Tokyo. Has worked at the National Research Institute for Metals (NRIM; currently NIMS) since 1991. Became a unit leader in 1999 at the Extremely-High Vacuum Station. Became a sub-leader at the NIMS Nanomaterials Laboratory in 2001. Became a director at the Advanced Nano Characterization Center in 2006. Became a nanotechnology field coordinator in 2010. Assumed the current position as the director of the Advanced Key Technologies Division in 2011.



Spin Detection of Monoatomic Surface Layers

Group Leader, Spin Characterization Group,
Nano Characterization Unit,
Advanced Key Technologies Division
Yasushi Yamauchi

Spin Characterization Group,
Nano Characterization Unit,
Advanced Key Technologies Division
Mitsunori Kurahashi

Spin Characterization Group,
Nano Characterization Unit,
Advanced Key Technologies Division
Han Zhang

Ultimate surface sensitivity enabled by slow atomic beams

A helium (He) atom has two electrons. When a metastable He atom, in which one of these electrons is excited to the higher energy state, impinges on the material surface, the electron with higher energy (about 20 eV) will be ejected. By keeping the He atom's kinetic energy level low down to a thermal energy level below 0.1 eV equivalent to that of helium gas in balloons, the He atom will rebound several angstrom outside of the material surface and will not penetrate the surface layer.

Due to this phenomenon, electrons ejected by a slow metastable He atomic beam irradiation of the material surface, gain information from the outermost surface layer only and thus they provide an ultimate "surface-sensitive property."

Electron spin in the outermost nickel layer

By selecting metastable He atoms, in which all spins of their paired electrons are aligned in the same direction, you can identify the spin direction (either upward or downward direction) of the surface electrons since only the surface electrons having the spin direction opposite to that of the He electrons interact with the He electrons (according to the Pauli exclusion principle).

The upper graph in Fig. 1 depicts spin asym-

metries calculated by the formula, $(I_p - I_a)/(I_p + I_a)$, where I_p and I_a represent intensities of electrons ejected from the clean surface of Nickel (Ni), a kind of permanent magnet, during a metastable He atomic beam irradiation with the parallel and antiparallel spin to that of the total Ni electrons (i.e., majority spin).^[1]

Because of the fact that interacting surface electrons and the electrons of metastable He atoms have to have spins in opposite directions to each other, the positive spin asymmetry at the Fermi level of 13.5 eV indicates that the spin direction of the surface electrons tends to be opposite to the majority spin (polarization). This spin reversal is normally found in ferromagnetic transition metals and accordingly, the electrons that pass through Ni are also polarized toward the opposite spin direction with respect to the majority spin.

Electron spin reversal in graphene monoatomic layer

A clean Ni surface was then exposed to benzene vapor to grow a graphene monolayer which has the appearance of a honeycomb consisting of hexagonal carbon atoms. The lower graph in Fig. 1 shows the resultant spin asymmetry ratios.^[1] At 14-15 eV, which is close to the Fermi level, the spin asymmetries are negative, indicating that by coating the Ni substrate with a graphene monolayer the surface spin is reversed and that the sur-

face electrons are polarized in a direction consistent with the majority spin.

These results have revealed for the first time that the contact of graphene with Ni causes spin polarization of the electron, which is relevant to electrical conduction but which originally shows no spin polarization. The theoretical calculations presented in Fig. 2 also support these results.^[2]

Development of high-precision state control technology

In this project, we are also developing molecular beams which are aligned in a single quantum state concurrently with the development of atomic beams. We have already developed oxygen molecular beam technology in which the direction of the molecular axis and spin can be specified. Using this technology, we have been able to resolve the decades-long mystery of the dynamics in aluminum oxidation reaction.^[3] In addition, we are currently developing technologies for low energy fine-focused electron beams and observation of the spatial distribution of electronic spin in the outermost surface layer.

[1] S. Entani, M. Kurahashi, X. Sun and Y. Yamauchi, CARBON 61. (2013). 134.

[2] X. Sun, S. Entani, Y. Yamauchi, A. Pratt and M. Kurahashi, J Appl. Phys. 114. (2013). 143713.

[3] M. Kurahashi and Y. Yamauchi, Phys. Rev. Lett. 110. (2013). 246102.

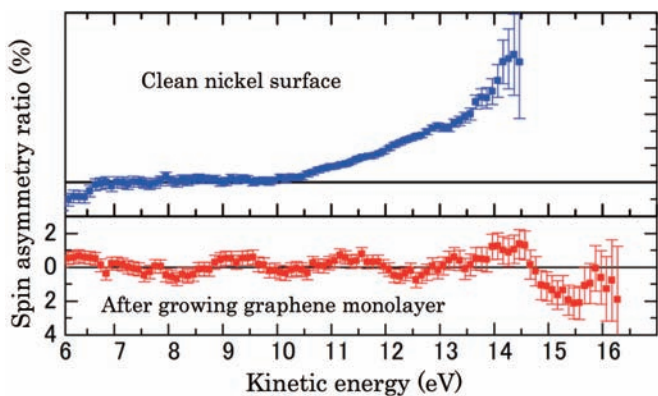


Fig. 1 Kinetic-energy-dependent spin asymmetries of electrons ejected from the surfaces of Ni (upper graph) and a graphene monolayer grown on it (lower graph).

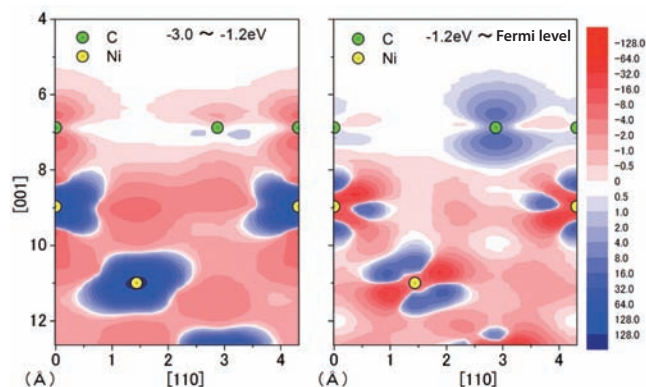


Fig. 2 Cross-sections of spin density distribution based on the first principle calculation. Blue areas represent the polarization of Ni toward the majority spin, while red areas stand for the opposite. At around the Fermi level (right), the electrons orbiting around the nuclei of carbon atoms (C) in graphene are polarized parallel to the majority spin of Ni. In contrast, at the lower level (left), the electrons orbiting around the nuclei of Ni are polarized antiparallel.

Profile

Yasushi Yamauchi Doctor of Engineering. Completed the graduate program at Osaka University in 1985. Joined NIMS in the same year. Currently studying surface spin after some experiences on ion beams, fusion reactor walls and X-ray computed tomography. / **Mitsunori Kurahashi** Doctor (Engineering). Chief researcher. Completed the graduate program at Kyoto University in 1996. Joined NIMS in the same year. Areas of expertise: surface science, magnetism, development and application of state aligned molecular beams. / **Han Zhang** Ph.D. Researcher. After graduating from Tsinghua University, completed the graduate program at the University of North Carolina in 2006. Assumed the current position at NIMS in 2013 after working as a JSPS (Japan Society for the Promotion of Science) researcher and an ICYS (NIMS International Center for Young Scientists) researcher. Currently studying nanowires and high-brightness electron beam sources.

Observation of Dynamic Behavior of Electrons in a Material — Development of New Technology for Chemical State Analysis —

Group Leader, Surface Chemical Analysis Group,
Nano Characterization Unit,
Advanced Key Technologies Division
Hideki Yoshikawa

Surface Chemical Analysis Group,
Nano Characterization Unit,
Advanced Key Technologies Division
Sei Fukushima

Surface Chemical Analysis Group,
Nano Characterization Unit,
Advanced Key Technologies Division
Shigeo Tanuma

Surface Characterization Group,
Nano Characterization Unit,
Advanced Key Technologies Division
Kunie Ishioka

Observation of chemical bonding in a material by detecting electrons excited by various wavelengths of light

The chemical bonding of atoms in a material is created by valence electrons. Observing the dynamic transitions of electrons between their energy levels enables us to ascertain the chemical bonding and its origin by which material is characterized. Furthermore, clarifying the chemical bonding states of various materials is essential for developing materials and improving the performance of new devices.

Photo-irradiation is commonly used as a probe to observe the behavior of electrons in a material because photons excite electrons in the material more directly than any other probes and enables energy-level selective excitation.

We can extract electrons from a material into the vacuum by irradiating it with short-wavelength light (ultraviolet rays and X-rays), which has greater energy than visible light, and we can produce excited states of electrons within a material by irradiating it with long-wavelength light (visible light, infrared light, microwaves).

The analysis of electrons extracted from a target element within the material into the vacuum by short-wavelength light enables to reveal the chemical bonding structure around target element, and observing the energy transfer

from electrons excited by long-wavelength light to the collective vibration of atoms (phonons) enables to reveal the direction and strength of chemical bonding in the material.

Nano-level depth-profile analysis using X-ray-excited photoelectrons

Observation of electrons extracted from a material by X-ray irradiation, called X-ray photoelectron spectroscopy, has been widely used in industry as a key chemical analysis technology. Because high-kinetic-energy electrons excited by X-rays, often transfer their energies to the material while traveling within it, only a few electrons escape the material with initial kinetic energy. This limits the observation depth using this method from several nanometers to tens of nanometers.

For this reason, X-ray photoelectron spectroscopy is categorized as a surface analysis method. The surface sensitivity enables to observe depth-profile of the chemical state of a nanometer multi-layered material. If we closely study the energy transfer from high-kinetic-energy electrons to a material and compile the findings into a database, we can accurately perform depth-profile analysis of the chemical bonding state within the specimen in sub-nano-level depth resolution. It targets the development of

various devices with nano-level internal structures (Fig. 1).

Ultrafast optical response determines performance of optoelectronic devices

In our daily life, we are surrounded by photonic materials, which work as photo-catalysts, solar cells, LEDs, lasers, etc. The optical functions are associated with microscopic processes such as the photo-excitation of electron-hole pairs, their energy relaxation, transport and radiative recombination. The efficiency of the photonic materials often relies on the time scales, typically between femtoseconds and microseconds.

We study ultrafast optical responses of the photonic materials by using a pump-probe technique. Femtosecond (10^{-15} second) optical pulses induce coherent phonons (Fig. 2) in the materials, with which we can monitor the collective atomic motions in the real time and extract information on the time-dependent electron-phonon coupling.

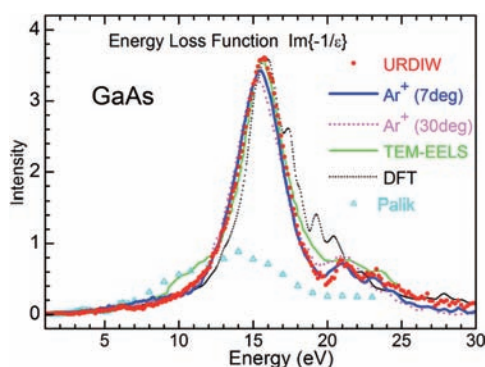


Fig. 1 The energy loss functions of gallium arsenide (GaAs) obtained in reflection electron energy loss experiments. When high-kinetic-energy electrons travel within a material, they cause collective excitations within the material. This phenomenon is called plasmon (the peak in the figure represents the plasmon of GaAs). It is a major factor that decelerates high-kinetic-energy electrons. Quantitative understanding of this phenomenon leads to precise estimation of the observation depth of X-ray photoelectron spectroscopy.

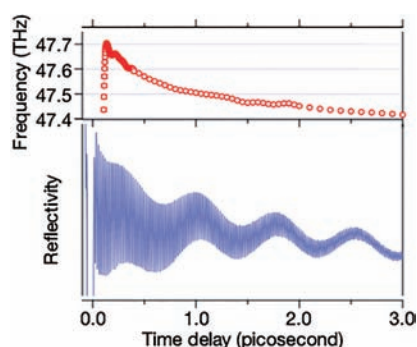


Fig. 2 The reflectivity of graphite is modulated periodically by coherent phonons (lower panel). The phonon frequency transiently upshifts upon photoexcitation (upper panel), revealing the electron-phonon decoupling in the two-dimensional system.

Profile

Hideki Yoshikawa Ph. D (Engineering). Completed his graduate study at Osaka University in 1992. Joined the National Institute for Research in Inorganic Materials (NIRIM; currently NIMS) in 1995. Specializes in X-ray photoelectron spectroscopy and electron scattering simulation. / **Sei Fukushima** Ph. D (Engineering). Completed his graduate study at the University of Tokyo in 1986. Joined NIRIM in 1994. Specializes in state analysis via inner shell electron theory, X-ray photoelectron spectroscopy. / **Shigeo Tanuma** Ph. D (Science). Completed the doctoral course at the University of Tsukuba, Department of Chemistry in 1982. Joined NIMS in 2001. Director of the Research Network and Facility Services Division, Leader of the Surface Chemical Analysis Group, and Director of the Materials Analysis Station as of March 2014. Specializes in surface analysis, surface electron spectroscopy. / **Kunie Ishioka** Ph. D (Science). Became NIRIM Researcher in 1994 and has held the office of Principal Researcher since 2006. Specializes in ultrafast semiconductor spectroscopy.



Application of Advanced Electron Microscopy for Characterization of Various Materials

Electron Microscopy Group,
Surface Physics and Structure Unit,
Advanced Key Technologies Division
Koji Kimoto

Microstructures and trace elements affecting macroscopic material characteristics

Superior material performance and characteristics of new materials are often determined by microscopic crystal structures or trace amounts of added elements. This is true not only for electronic devices that are increasingly miniaturized such as semiconductor devices and magnetic disks, but also for functional materials such as fluorescent materials used for LEDs, or structural materials such as steel used for buildings. Macroscopic characteristics of these materials, such as their luminescence property and mechanical strength, change dramatically by added elements. By applying electron microscopy to identify microstructures and trace elements that exhibit material functions, we can push forward development of high-performance materials even further. NIMS develops advanced measurement techniques using electron microscopy, and promotes research on material characterization in cooperation with internal and external material researchers including those from other research institutes and companies.

Cutting-edge electron microscopy

The minimum size of the structure that can be observed by electron microscopy (spatial resolution) depends on the wavelength of the electrons (normally several picometers) and the aberrations of the lenses used in the observation.

With a spherical aberration corrector that has been put to practical use recently, it is possible to observe materials by converging electrons to a size smaller than the atomic diameter (approximately 0.1 nanometers). Since electrons entering a sample scatter through various interactions with atoms in the material, we can, for example, analyze elements and the chemical bonding state from the electron energy-loss upon the scattering. In addition, we can use the characteristic of electrons being both waves and charged particles to measure magnetic or electric fields.

Electron microscopy research at NIMS

Figure 1 shows the appearance of an electron microscope we currently use. In order to realize atomic resolution, the microscope is installed on an active anti-vibration system in a room with a panel air conditioner. Users operate the microscope from the next room separated by a double window. Spatial resolution of 50 picometers is achieved by using a spherical aberration corrector, and we can directly observe crystal structures. Moreover, with energy resolution of 70 meV realized by a monochromator, we can analyze the electronic structure and identify the valence and the coordination number of the constituent elements.

We also develop software for experiments and analyses, and develop technologies for handling materials that alter with the slightest amount of moisture. The developed technologies are also

used for collaborations with external researchers through projects such as the NIMS Microstructural Characterization Platform.

Example of advanced measurement

Here is one example of NIMS's diverse material development and characterization efforts.

Figure 2 shows an example of detection of europium (Eu) in SiAlON, which NIMS has developed as a fluorescent material for LEDs. We can see that an Eu monoatom exists in a tunnel with a diameter of about 0.5 nanometers within the crystal structure. This result was obtained by using custom multiple measurement software and succeeding in detecting the slight signals generated by the monoatom. Figure 3 shows the result of observation of vortex-like microscopic magnetic domains called Skyrmions by Lorentz microscopy.* Observation of magnetic domains of a nanometer order is effective for analyzing magnetic memory devices using electron spin as magnetic information.

In this manner, we are currently advancing research and development of electron microscopes not as mere magnifying glasses, but as comprehensive tools for analyzing material characteristics.

* Lorentz microscopy: One of the measurement techniques of electron microscopy for observing microscopic magnetic domains by using a Lorentz force in the magnetic field.



Fig. 1 (a) Appearance of an electron microscope. Picture of a user operating the microscope from the next room is on the page 2-3.

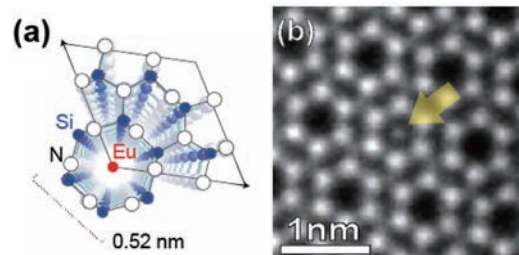


Fig. 2 (a) Crystal structure of SiAlON fluorescent material. (b) The Eu monoatom dopant observed (pointed to by the arrow in the center); measured under accelerating voltage of 80 kV; the sample provided by Hirosaki (NIMS), et al.

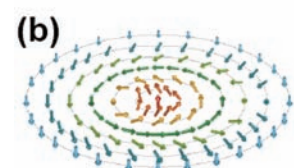
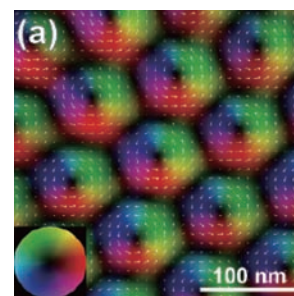


Fig. 3 (a) Example of observation of Skyrmions generated within FeGe by Lorentz microscopy. (b) Schematic of a Skyrmion.

Profile

Koji Kimoto Ph.D. (Science, Tohoku University). Completed the master's course in the Graduate School of Engineering, Nagoya University, in 1989, and joined Hitachi Research Laboratory, Hitachi, Ltd., in the same year. Became a Senior Researcher of the NIRIM (currently NIMS) in 1999. Also teaches at Kyushu University, since 2009, as a professor under the Joint Graduate Program with NIMS.

Development of High Field Solid State NMR Technology and Its Application to Material Analysis

Group Leader, High Field NMR Group,
Advanced Nano Characterization Center
Tadashi Shimizu

Efforts to promote the use of NMR technology in inorganic material studies

NMR (nuclear magnetic resonance) is a well-established technology in organic chemistry and clinical medicine (e.g., magnetic resonance imaging or MRI) used in standard analytical instruments. However, it is not a common technology used in material research.

In both organic chemistry and MRI, NMR signals from hydrogen are measured. The magnetic field strength used in organic chemistry is about 10T (tesla) and that used in MRI ranges from 1T (body parts other than the head) to 4T (brain). While these magnetic fields are relatively low given that superconducting magnets can generate higher magnetic fields, the demand for higher magnetic fields is generally low. That is because hydrogen is often the only element required to be measured in organic chemistry and MRI.

Because NMR signals from hydrogen are stronger than those from any other elements, they can be measured even in low magnetic fields. However, there is a problem with the application of NMR technology to material studies. Most inorganic materials in particular do not contain hydrogen, so if the technology is to be used in inorganic material studies, it will be necessary to measure NMR signals from other elements that generate weaker NMR signals. Since the sensitivity and resolution of NMR signals increase in higher magnetic fields, the use of a sufficiently high magnetic field is necessary in order to accurately measure elements with weak NMR signals.

In theory, NMR technology is applicable to about 80% of the elements in the periodic table. However, in reality, NMR signals from only a few

elements such as hydrogen had been measurable due to the delayed progress in the development of high field magnets. Thus, NMR technology had been useful only in limited research areas such as organic chemistry.

The most effective method to expand the applicability of NMR technology is to use a high magnetic field. While the strength of the magnetic fields used with common NMR analytical instruments is about 10T, the use of magnetic fields with strength greater than 20T helped achieve the first successful application of NMR technology to elements which had been the least applicable, known as quadrupolar nuclei (i.e., atomic nuclei that have a nuclear spin quantum number greater than one), which account for about 60% of the elements in the periodic table (Table 1).

Traditionally, it had been known that quadrupolar nuclei are extremely difficult to resolve using NMR technology and that the use of a high magnetic field is technically the only solution to this problem. If the development of high field solid state NMR technology enables accurate measurement of quadrupolar nuclei, it would be applicable to a wide range of material studies including those on inorganic materials. Since NMR technology has an advantage of being rather effective in the analysis of random structures in amorphous materials, it is expected to work complementarily with conventional technologies such as X-ray and electron microscopy.

World's first successful high-resolution measurements of Ca, Mg, Ti and Mo in practical materials

Figure 1 shows a graph which compares the degrees of difficulty in measuring NMR among quad-

rupolar nuclei. The dotted lines indicate the strength of the magnetic field necessary to analyze NMR signals from a given element (i.e., elements located closer to the lower right corner require higher magnetic fields). Red circles indicate quadrupolar nuclei from which NMR signals have been successfully measured in the past five years using the 930MHz-NMR facility (using a 21.8T magnetic field) which is in operation at NIMS.

Notably, we succeeded for the first time in the world in high resolution measurement of NMR signals from Ca, Mg, Ti and Mo in practical materials, which are among the most difficult elements to measure. NMR signals from these elements had been undetectable using the conventional facilities with magnetic field strength of about 10T.

Although we can now measure NMR signals from those difficult elements, the measurement is time-consuming, requiring us to spend more than 100 hours duplication measurements. We spend the first several days of the experiment patiently choosing the proper parameters to use out of 20 parameters representing various measurement conditions. This process requires experience and insightful skills to perceive "virtual signals" and highly specialized knowledge.

Solid state NMR technology applicable to quadrupolar nuclei has become available only recently after the invention of magnets that can generate 20T or higher fields. Since nearly no references or literature on this subject are available, we feel like we are groping in the dark when working on this new technology on a daily basis. At the same time, we are excited to explore it. We hope to expand the applicability of solid state NMR facilities to measure various new substances and materials beyond their traditional application in organic chemistry.

Dipole nuclei																		Quadrupolar nuclei																																																																																							
$I = 1/2$																		$I > 1$																																																																																							
H	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra	Ac	Ku	Ha	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Table 1. The sensitivity and resolution of dipole nuclei (blue) are directly proportional to the applied magnetic field. The sensitivity and resolution of quadrupolar nuclei (red and yellow) improve by raising the magnetic field strength to the second to fifth power. Since magnetic field strength of more than 20T is required to acquire high NMR resolution when applied to quadrupolar nuclei, the conventional NMR devices (with about a 10T magnetic field) were not useful in analyzing them. (T. Shimizu, et al., Chem. Lett. 33 (2004) 1502)

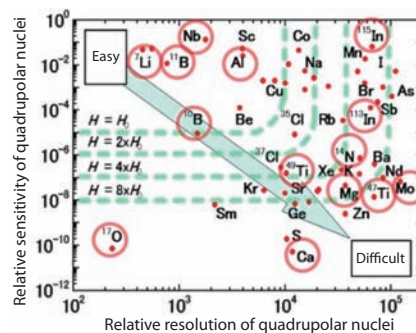


Fig. 1 A graph indicating the degrees of difficulty in measuring NMR among quadrupolar nuclei. The dotted blue lines indicate the extent to which NMR signals from elements are measurable in relation to magnetic field strength. Red circles indicate quadrupolar nuclei from which NMR signals had been successfully measured using a 930MHz-NMR facility. (T. Shimizu, et al., Chem. Lett. 33 (2004) 1502)

Profile

Tadashi Shimizu Doctor of Science. Assistant Researcher at The University of Tokyo, Institute for Solid State Physics from 1987. Joined NIRM in 1990, and current position from 2001.



Development of High-Pressure Cell to Neutron Scattering Experiments and Their application to Multiferroic Materials

Unit Director,
Quantum Beam Unit,
Advanced Key Technologies Division
Hideaki Kitazawa

Neutron Scattering Group,
Quantum Beam Unit,
Advanced Key Technologies Division
Noriki Terada

Understanding physical properties of materials based on electronic states

Because neutrons, constituents of atomic nuclei, possess high penetrability and great responsiveness to light elements and spin states, the application of neutron beams to advanced materials reveals material's internal structures such as composition, texture and various microscopic states (e.g., electronic, spin and chemical states) in a non-destructive way. We have been developing equipments that are able to create various multiple extreme environments (e.g., high pressure, low temperature and high magnetic field) in order to understand important electronic states of materials.

Relationship between multiferroics and magnetic structure

Multiferroics that possess several strongly ordered states (e.g., ferromagnetism [or antiferromagnetism], ferroelectricity and ferroelasticity) not only exhibit unique and interesting physical phenomena but also indicate that magnetization and dielectric polarizationⁱ can be manipulated by electric field and magnetic field, respectively. Due to these properties, multiferroics are attracting the attention of researchers who develop devices such as new types of large scale memory devices. The delafossite CuFeO_2 with a layered triangular lattice was studied at an early time as a model for frustrated magnetismⁱⁱ, and it has been studied extensively in

recent years as a multiferroic model after the discovery of magnetic-field-induced ferroelectric polarization¹.

As illustrated in Figure 1, magnetic frustration of CuFeO_2 is released by spontaneously distorting its crystal lattice at low temperatures (i.e., its wavenumber changes with temperature), and thereby the magnetic structure with the commensurateⁱⁱⁱ magnetic wave vector and without dielectric polarization is realized. The commensurate magnetic state can easily change to a ferroelectric state with the incommensurate magnetic phase² by means of impurity substitution. This suggests that commensurate states are extremely unstable, and there seems to be a strong relationship between the commensurate-incommensurate magnetic structure and ferroelectricity.

In this research, we anticipate that magnetic structure can be changed by applied pressure suppressing the spontaneous lattice distortion. We have developed a hybrid anvil high pressure cell which allows us neutron diffraction experiments under high pressure. Recently we carried out neutron diffraction experiments using the high pressure cell.

High pressure cell for neutron diffraction experiments and magnetic structure under high pressure

The hybrid high pressure cell (Figure 2), which we developed with Dr. Toyotaka Osakabe of the Japan Atomic Energy Agency for use in pulsed neutron diffraction studies, is not only capable of generating high pressure but is also equipped with a

hybrid anvil cell consisting of SiC (silicon carbide) and WC (tungsten carbide) anvils, allowing the neutron beams detectable widely³. Conventionally, it had been difficult to attain sufficiently large signal-to-noise ratios (S/N) due to scattered neutrons from a high pressure region and we resolved this problem by greatly improving the S/N ratio using a BN (boron nitride) masking shield.

As shown in Figure 1, we found that under high pressure at 7.9GPa (= 79,000 atmospheric pressure), CuFeO_2 maintains an incommensurate magnetic structure even at low temperatures, which was not the case under 1 bar (= 1 atmospheric pressure)³

In other words, under high pressure, a frustrated magnetic ordered state is stably preserved at low temperatures.

These results indicate that we might be able to manipulate multiferroic properties by adjusting the pressure, as such manipulation was feasible when magnetic fields and chemical substitution were tuned. For future studies, we plan to carry out detailed neutron experiments under high pressure, aiming to reveal the mechanism behind the expression of multiferroic properties under such conditions.

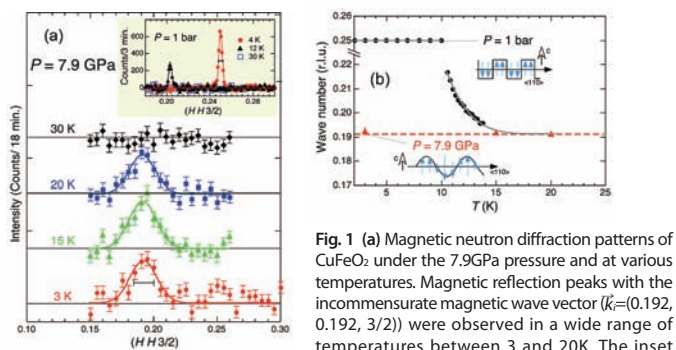


Fig. 1 (a) Magnetic neutron diffraction patterns of CuFeO_2 under the 7.9GPa pressure and at various temperatures. Magnetic reflection peaks with the incommensurate magnetic wave vector ($k_z=0.192, 0.192, 3/2$) were observed in a wide range of temperatures between 3 and 20K. The inset compares magnetic neutron diffraction patterns among different temperatures under 1 bar. The wavenumber indicates temperature dependence and the magnetic reflection peaks with the incommensurate magnetic wave vector k_z shift to those with the commensurate magnetic wave vector ($k_z=1/4, 1/4, 3/2$) at a low temperature of 4K. (b) Temperature dependence of the wavenumber and anticipated magnetic structures compared between 1 bar and 7.9GPa.

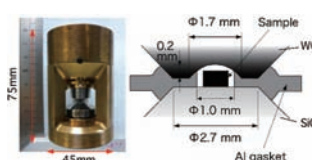


Fig. 2 Hybrid high pressure cell for neutron scattering experiments (diameter: 45mm, height: 77mm). (Left) Whole image of device. (Right) Close-up of a hybrid anvil part. The upper and lower anvils were made of tungsten carbide (black) and silicon carbide (light blue), respectively. The actual dimension of the specimen is about 0.5mm x 0.6mm x 0.25mm, and glycerin is used as a pressure medium.

- 1) T. Kimura et al., Phys. Rev. B 73, 220401(R) (2006).
- 2) N. Terada et al., Phys. Rev. B 78, 014101 (2008).
- 3) T. Osakabe et al., J. Phys. Soc. Jpn., 79 034711 (2010).
- 4) N. Terada et al., Phys. Rev. B 83, 020403(R) (2011).

i Dielectric polarization: It is also known as electric polarization. Polarization of electric charge occurs when an electric field is applied to a dielectric material. Dielectric polarization that occurs in the absence of an external electric field is called spontaneous polarization (or ferroelectric polarization).

ii Frustration: The strongest frustrated state occurs when spins of adjacent magnetic atoms on a triangular lattice interact so that their spins only align in opposite directions each other (antiferromagnetic exchange interaction) as shown in the left diagram of Figure A. If the direction of spin 1 is arranged upward, the direction of spin 2 must become downward. Thereby the direction of spin 3 cannot choose either upward or downward directions (frustration). When the spin direction of each magnetic atom in the triangular lattice is allowed to rotate freely, the frustration state is partially weakened as shown in the right diagram of Figure A. This mechanism may lead to the emergence of ferroelectric polarization.

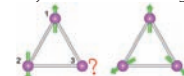


Figure A. Magnetic frustration with a triangular lattice

iii Commensurate and incommensurate: If a period of a certain order is an integer multiple of the lattice constant, it is called commensurate. On the other hand, if the period is a non-integer multiple of the lattice constant, it is called incommensurate.

Profile

Hideaki Kitazawa Completed the physics curriculum at the Graduate School of Sciences, Tohoku University, in March 1987. Employed as a researcher at the Institute of Physical and Chemical Research in April 1987. Became a chief researcher at the National Research Institute for Metals in 1995. Became a group leader at NIMS in April 2001. Assumed the current position in April 2011. Acquired doctoral degree in science in 1988. / **Noriki Terada** Completed the doctoral program in physics at the Graduate School of Science, Tokyo University of Science, in March 2006. Became a basic science special researcher at the Institute of Physical and Chemical Research. Assumed the current position in April 2007. Studied at the Rutherford Appleton Laboratory ISIS in the United Kingdom between August 2011 and February 2014 taking advantage of the JSPS (Japan Society for the Promotion of Science) program.

Characterization of Buried Interfaces Using Synchrotron Radiation Measurement

X-Ray Physics Group, Quantum Beam Unit,
Advanced Key Technologies Division

Kenji Sakurai

Characterizing buried interfaces

It is a general practice in nanotechnology research and development to cover nanostructure surfaces, which were fabricated under precise control, in order to protect it from physical or chemical deterioration and damage. It is also common to create multilayered nanostructures.

The properties and functions of the parts on the surface of the most interest, which are kept unexposed by covering the surface with a different substance, have been studied and utilized. What is known as “buried interfaces” include not only semiconductors, magnetic devices and thin films used of soft materials but also various coating interfaces, adhesive interfaces, interfaces between two different substances and solid-liquid interfaces that can be found in ecosystems, quasi-ecosystems and battery materials.

Many advanced characterization and analytical technologies are becoming very useful in detailed analysis of atomic arrangements, molecular-level structures and electronic states on exposed surfaces. However, it had been difficult to apply these technologies to buried interfaces.

Sophistication of X-ray reflectivity method

At NIMS, we have been developing the technology called X-ray reflectivity and enhancing the analytical method to characterize the various kinds of interfaces mentioned above.

Our first specific objective is to pioneer a model-free analytical method which is effective in dealing with the case where the interface structure is complex and thus difficult to understand in detail, the case where interfacial reaction might cause the production of an additional layer or the loss of an existing layer, and the case where analysis using a structural model is not very reliable. Accordingly, we have been planning and implementing a new analytical method which does not rely solely on fitting of structural parameters to the data but instead uses transformation schemes such as the Fourier transform and wavelet transformation.

Our second objective is to develop the technology to form an image based on the distribution of electron density at a certain depth in an interface (Fig. 1). In the field of medicine, X-ray computed tomography is frequently used to attain cross-sectional images of the brain and other internal organs in a non-destructive man-

ner. Similarly, we are developing a methodology to analyze internal structures buried under thin films and multilayer films using reflected X-rays rather than penetrating X-rays (patent application submitted). In addition, we found that white synchrotron radiation is also effective for this purpose (Fig. 2).

Our third objective is to develop technology to track the changes in interfaces which continuously change. In order to identify the mechanism responsible for interfacial reactions and specific functions of interest, it is extremely important to conduct real-time measurement of changing interfaces in addition to static measurement.

Research and development activities to enhance the abovementioned characterization and analytical technologies are expected to advance greatly due to emerging tools such as a new source of ultra-low emittance synchrotron radiation and an X-ray free-electron laser that will become available soon. So in the near future, we expect to be able to characterize many interesting phenomena that occur in buried interfaces in detail and in a more direct manner.

Reference: Sakurai, K. (editor) 2009. Introduction to X-ray reflectivity. Kodansha Scientific Ltd, Tokyo, Japan.

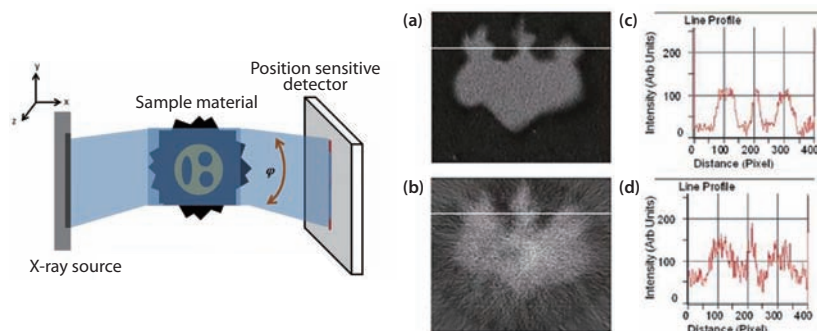


Fig. 1
The upper diagram illustrates the mechanism behind the imaging of superficial and buried interfaces using X-ray reflectivity. This approach revealed that imaging of electron density distribution along the parallel direction of the interface at an intended depth can be achieved by first acquiring a strength profile of the reflected X-rays and then mathematically processing it to create a reconstructed image. The images and graphs in the right show the results concerning the pattern of gold coating on a silicon surface. (a) Image of gold coating pattern observed using an optical microscope, (b) Line profile corresponding to the image in (a), (c) Reconstructed image based on X-ray reflectivity projection data, and (d) Line profile corresponding to the image in (c).

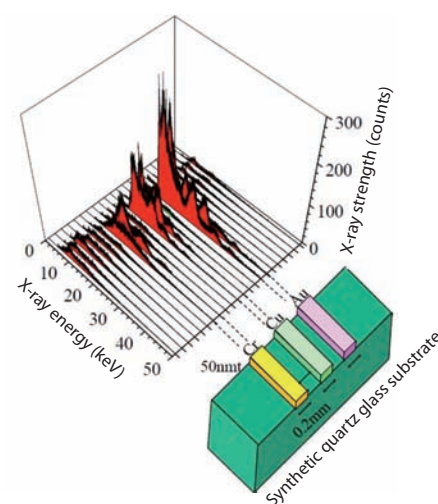


Fig. 2
One-dimensional X-ray reflectivity scanning of Cr, Cu and Au line patterns fabricated on a glass substrate. Localized analysis of an interface can be achieved by identifying each line pattern through the continuous acquisition of X-ray reflectivity spectra at specified points while moving the sample material, using parallel and microfocus beams of high energy white X-rays.

Profile

Kenji Sakurai Doctor of Engineering. Graduated from the Faculty of Engineering, the University of Tokyo, in 1983. Completed the doctoral program at the University of Tokyo graduate school in 1988. Joined NIMS in 1988. Currently a leader at NIMS' X-Ray Physics Group in the Quantum Beam Unit.

NIMS NEWS

1

MoU with Southeast University in China for fuel cell electro-catalysts and electrodes

On March 10, NIMS and Southeast University (SEU) in China concluded memorandum of understanding (MoU) for international collaboration which is for design of graphene based materials as new platinum free electro-catalysts and development of high quality fuel cell electrodes. SEU located in Nanjing is one of the oldest institutions of high education and scientific research in China. Its origin can be traced back to 1902. The university boasts over 34 schools or departments with 64 undergraduate disciplines in all, which offers 98 Ph.D. programs

and 208 Master programs. The total number of faculty and staff is 6,000, including 1,300 full or associate professors. A key person of SEU side is Prof. Yuanjian Zhang who spent some important years in NIMS as a young scientist. After the MoU ceremony, Prof. Zhang talked his recent work in his seminar to strengthen the tie of both institutions. Since NIMS is located in Tsukuba city, Tsukuba University will join this international collaboration team. It is expected that aforementioned research team will create lots of outcomes to develop the high quality elec-

trodes in fuel cell and contribute to the materials science in both countries.



Participants at the signing ceremony (from top left): Dr. Mori, Prof. Liu, Prof. Sun, Prof. Zhang, Dr. Takada.

2

Consort of the Father Emir of the State of Qatar, Her Highness Sheikha Moza Visits NIMS

On April 22, Her Highness Sheikha Moza bint Nasser, Chairperson of Qatar Foundation for Education, Science and Community Development (QF) visited NIMS on the occasion of her visit to Japan. Her Highness was accompanied by His Excellency Mr. Yousef Mohamed Bilal, Qatar's Ambassador to Japan and a high-level scientific delegation, including President of QF Research and Development Mr. Faisal Alsuwaidi and Executive Director of the Qatar Environment and Energy Research Institute (QEERI),

Dr. Mohammad Khaleel. Her Highness and the delegation received a presentation about NIMS and its work in the filtering and purification of water research, and the supercomputer, K computer. Her Highness had a discussion with President Prof. Ushioda and executives regarding bilateral research collaboration. Both sides explored potential synergies in materials technology for energy and environment issues between NIMS and QF, especially QEERI. The meeting concluded with the signing cere-

mony of a Memorandum of Understanding to encourage joint research activities.



group photo.

Hello from NIMS

Dear NIMS NOW readers,

I was born in Indonesia and moved to New Zealand when I was 14 years old. I am very blessed to have two wonderful countries in



Climbing Mt. Fuji, the tallest mountain in Japan.

which I can call home. After finishing my PhD study from The University of Auckland, I started working as a postdoctoral researcher in Toyohashi University of Technology, Japan in May 2010. A year after that, I got offered a position in the Photovoltaic Materials Unit of NIMS. Working at NIMS is very exciting. I truly enjoy the diversity in NIMS. Not only that I get to learn from the talented Japanese researchers, but also I have the opportunity to work with many international researchers. Research facilities are superb and definitely world-class. NIMS is located in Tsukuba city, which is a very comfortable place to live and it is only one hour away from the excitements of Tokyo. Living in Japan is an amazing experience. Japan is such a beautiful country that is rich



Sakura season, Tsukuba city.

in culture with very friendly and down-to-earth people. I am so thankful for this opportunity.



Noviana Tjitra Salim (Indonesia)
Period of Stay at NIMS: 2.5 years
Postdoctoral researcher,
Photovoltaic Materials Unit



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National Institute for Materials Science

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cover image: Very Low Temperature, High Magnetic Field Scanning Tunneling Microscope.

To subscribe, contact:

Dr. Kazuo Nakamura, Publisher

Public Relations Office, NIMS

1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047 JAPAN

Phone: +81-29-859-2026, Fax: +81-29-859-2017

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R100
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