NIMS NOW
International

Rare Earths
The Potential of NIMS

Hydrogen Magnetic Refrigerator

Rare Earths
The Potential of NIMS

Rare earths are elements which are scarce, but are also indispensable for modern society.

Although not widely known, recent social conditions in Japan have suddenly turned the spotlight on this group of elements.

Because an industrial structure which does not depend on the rare earths is now required, urgent efforts are being made to develop substitutes and other solutions to the rare earth problem.

Among these, NIMS, with its "element strategy," has attracted keen interest as a cutting-edge research center in the field of elements.

What are the rare earths, and what is the origin of their unique properties?

Are higher efficiency, and ultimately, rare earth-free technologies possible?

This issue of NIMS NOW introduces research related to the rare earths, featuring on the NIMS Center for Strategic Natural Resources.

photo: Neodymium magnet used for hard disk and rare earth compounds extracted from it.

Periodic Table of Elements

Rare Earths

Lanthanide

Actinide

Solid
Gas
Liquid
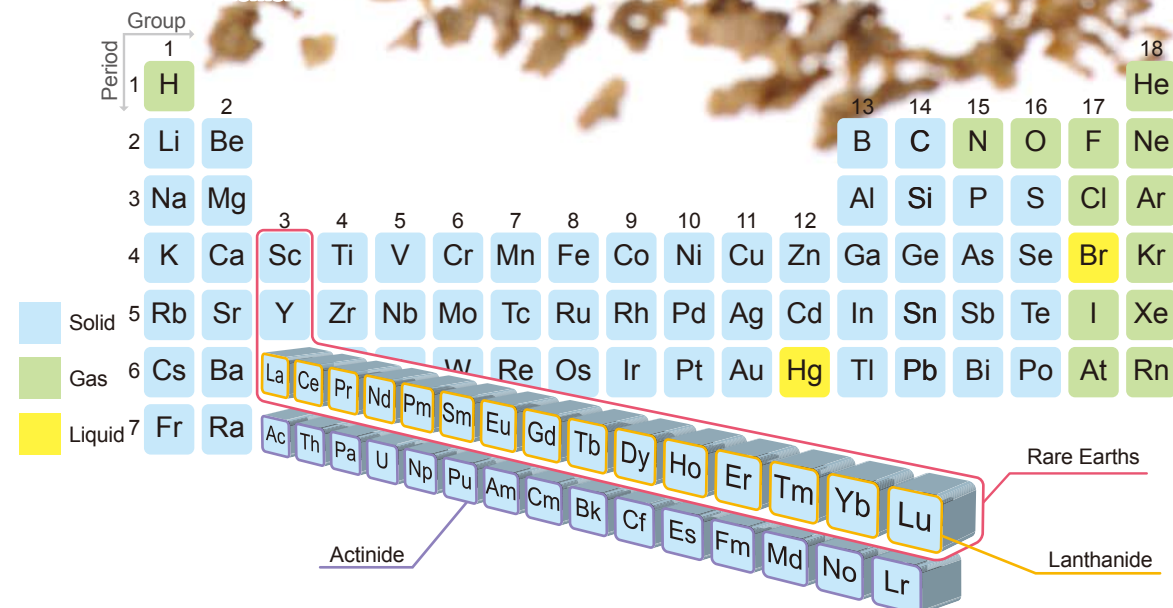
Research at NIMS in Search of Solutions to the Rare Earth Problem

Kohmei Halada, Managing Director
Center for Strategic Natural Resources

Spotlight on the rare earths.

The "rare earths" are elements that include the 15 elements La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu called lanthanoids, which belong to row 5 of Group 3 of the periodic table of the elements, and also Y and Sc, which are located higher in the periodic table in the same Group 3.

The rare earths are currently a focus of attention.

For example, as the strongest type of sintered magnets, neodymium (Nd) and dysprosium (Dy) have been widely used in small motors for automobiles, compressors for air conditioners, and similar applications for many years, but in the future, these rare earths may also be used in drive motors for electric vehicles and dynamos for wind power generation. As phosphors, the rare earths are indispensable in displays and LED lighting. Rare earths also have many other functions which are expected to find use in future applications such as magnetic refrigeration devices.

Why do rare earths have these special properties?

These are distinctive functions which originate from the "4f orbital" possessed by rare earths. It may be easier to understand from the periodic table, that when the atomic number increases by one, the number of electrons increases by one each in any of the orbits from 1 to 5.

In many other elements, increases in electrons occur from the outermost orbital. However, in the rare earths, these fill the 4f orbital. Furthermore, a 5s orbital and 5p also exist outside the 4f orbital, resulting in a state in which the electrons are already buried. This means that the 4f orbital is completely guarded by the outer orbitals. As a result, the rare earths display distinctive properties such as the effects of magnetism utilizing magnetic spin, fluorescence using the transition of the 4f electrons, and other features.

In addition to the properties which originate from these 4f electrons, the rare earths also have properties resulting from their atomic radius, charge, and so on. These properties are used in processing of ceramics and glass.

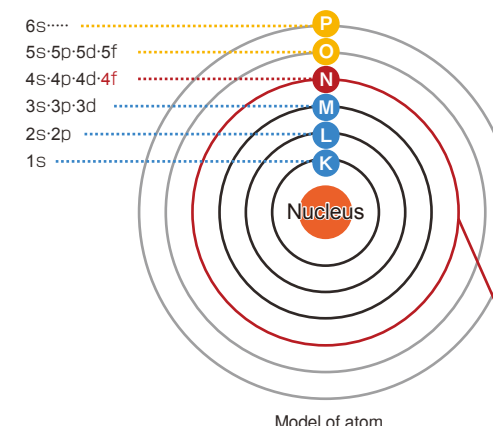**Effects of rare earth resources on the environment.**

These "multi-talented" rare earths will become increasingly necessary in our daily lives in the future. As this happens, the amounts and suppliers of these resources will become a concern. However, because the global reserves of rare earths are somewhat less than 100 million tons, while annual consumption is 120,000 tons, these elements are actually more plentiful than is generally imagined.

This being the case, why are limits on these resources expected? One reason is environmental limits. Refining of the rare earths is energy-intensive and has heavy environmental impacts. For example, a large quantity of waste liquid is generated in separating elemental rare earths from rare earth minerals. In many cases, the rare earths are found in coexistence with radioactive substances, and these must be removed.

Due to these environmental loads, rare earths cannot be produced except where the environmental cost is low. (The sole exception to this is dysprosium (Dy), which is only enriched in ion-absorption type deposits in southern China at present.)

Thus, the development of technologies for efficient utilization and circulation of these precious rare earths, as well as substitute technologies, is now urgently required.

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Normally, electrons embed in order from the inner to the outer shells, but in the lanthanides, electrons first enter from the O and P shells located on the outer side, and the 4f orbitals, which are in the N shell, embed thereafter.

Model of atom
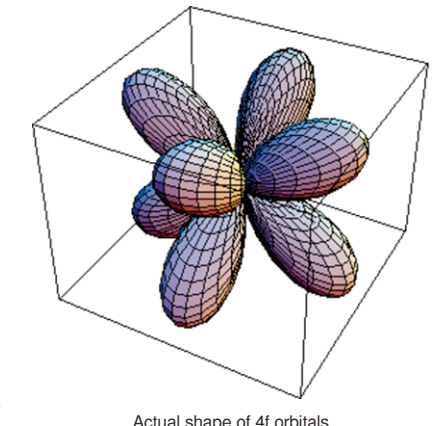
Actual shape of 4f orbitals

Element Strategy in Permanent Magnets
A Strategy for
Dysprosium-free Neodymium-based Magnets

Kazuhiro Hono
NIMS Fellow and Managing Director
Magnetic Materials Center

Why is dysprosium so critical?

To achieve high energy efficiencies in hybrid and electric vehicles (HV/EV) and wind generators, high performance permanent magnets must be used for motors and generators. A large amount of neodymium magnets that are composed of mainly iron (Fe), neodymium (Nd) and boron (B) is now used in these energy related applications. Until recently, the largest application of the neodymium magnets was voice coil motors that drive heads in hard disk drives, but it has shifted to traction motors for HV/EV recently, and this trend will continue in the future.

During the operation of motors and generators, the temperature of magnets increases to about 200°C. Although the neodymium magnets can exhibit the highest maximum energy products at room temperature among various permanent magnets, the coercive field against thermal demagnetization is relatively low at an elevated temperature. To overcome this weakness, the currently used neodymium magnets for HV/EV traction motors and wind generators contain a substantial amount of dysprosium, one of heavy rare earth elements[*] to substitute a part of Nd in the $Nd_2Fe_{14}B$ main phase. The natural resources of these heavy rare earth elements are very scarce, and production is limited only in a few countries. The risk of import restrictions of rare earth elements due to a political situation has recently become apparent. Although the natural resources of light rare earth elements are not so scarce if worldwide production is secured, the heavy rare earth elements are found only in a few limited regions in the world. Since the use of heavy rare earth elements in the neodymium magnets for HV/EV is more than 3 times larger than their natural abundance of Dy with respect to that of Nd, the supply of Dy may face difficulty in the near future if the same amount of Dy continue to be used.

Therefore, the development of neodymium magnets that can be used at 200°C without Dy is strongly desired. If the consumption of the heavy rare earth elements can be reduced to less than the natural abundance of Dy with respect to Nd (approximately 10%), the immediate problem of the shortage of Dy for HV/EV motors can be relieved. In the long run, the development of new high performance magnets that can replace the neodymium magnets is also desirable.

Commercial neodymium magnets

The neodymium magnet was developed by Sagawa and his colleagues in 1982 by applying a powder metallurgy process to Nd-Fe-B alloy, and is the world's highest performance permanent magnet even after 28 years of the invention. Because the main constituent phase of the magnet, $Nd_2Fe_{14}B$ (atomic composition: $Nd_{12}Fe_{82}B_6$), possesses a combination of high magnetization and magnetocrystalline anisotropy, neodymium magnets can realize the unrivalled maximum energy products.

The critical properties for the heat resistance of magnets are the Curie temperature of the compound and temperature dependence of coercive field against demagnetization, so called coercivity. One weak point of the $Nd_2Fe_{14}B$ phase is its comparatively low Curie temperature of 320°C (c.f. Curie temperature of iron: 770°C). In order to obtain adequate coercivity at an operating temperature of 200°C, 30% of the Nd is replaced with Dy in the high coercivity Nd magnets for HV/EV and wind generators. On the other hand, Dy addition reduces the maximum energy product due to the antiferromagnetic coupling between Dy and Nd. In other words, Dy addition increase the thermal resistance of the magnets at the expense of the maximum emery products. Ideally, we want to increases the coercivity of the magnets without losing the maximum energy products.

Coercivity improvement without Dy?

How can we improve the heat resistance or coercivity of neodymium magnets without using Dy? To answer to this question, we noted that the coercivity of commercial sintered Dy-free neodymium magnets is only 15% of the theoretical limit, i.e. the anisotropy field of the $Nd_2Fe_{14}B$ phase of ~76kOe. Coercivity is not an intrinsic physical value of the main constituent phase, but is an extrinsic value that varies depending on the microstructure of the material. As a simple principle, if the crystal grain size is refined to approximately 200nm, which is the single magnetic domain particle size, and the grains can be magnetically insolated by modifying the grain boundary chemistry with a nonmagnetic layer, it should be possible to achieve at least 50% of the theoretical limit, or about 30kOe, without using Dy.

## Multi-scale analysis of neodymium magnets at NIMS

To substantially increase the coercivity of sintered neodymium magnets, it is essential to understand the structure and coercivity relationships in currently available commercial magnets. The coercivity is controlled by nanoscale weak points in a global microstructure; therefore, it is necessary to characterize the microstructures ranging from the micron scale to the atomic scale. This type of multi-scale microscopy/analysis is not so easy. To cover the multiscalability of the critical structure that governs the coercivity of sintered magnets, we perform high resolution scanning electron microscopy (HRSEM), high resolution transmission electron microscopy (HRTEM), and three-dimensional atom probe (3DAP) analysis of commercial and experimental neodymium permanent magnets. **Fig. 2** shows SEM/TEM/3DAP analyses results of a commercial sintered neodymium magnet. The particles with the gray contrast is the crystal grains of the $Nd_2Fe_{14}B$ main phase. Brightly imaging particles are observed at the triple junctions of the grain boundaries of the main phase, which are Nd-rich phases. Although very faint, the boundaries between the main phase grains appear with a slightly brighter contrast. If nonmagnetic elements such as Nd can be enriched to these grain boundaries to form a thin grain boundary phase with a thickness of a few nm, each $Nd_2Fe_{14}B$ grain is expected to be magnetically isolated from neighboring grains. In addition, if the crystal grains of approximately 3μm can be refined to around 200nm, which is close to the single magnetic domain particle size, further enhancement of coercive force is expected.
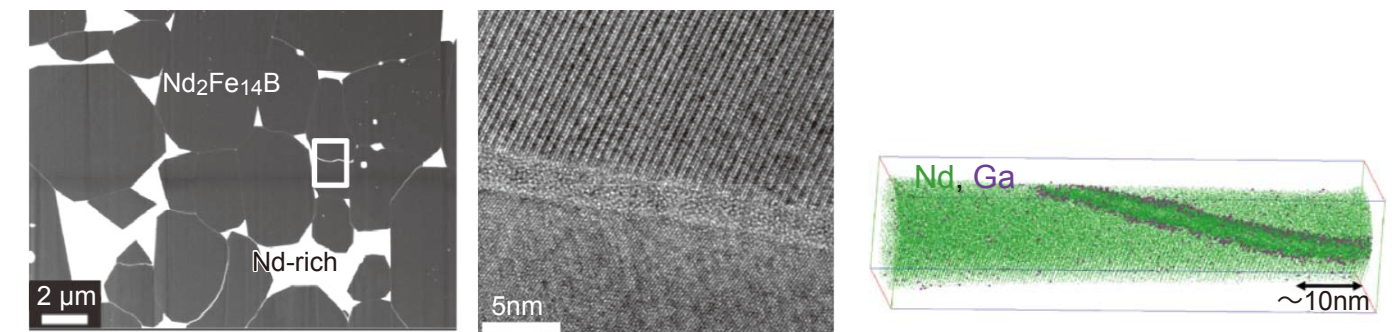
The achievements of substantially higher coercivity have recently been reported as results of the NEDO[**] "Rare Metal Substitute Materials Development Project" and the MEXT[***] "Elements Science and Technology Project." In these results, multi-scale analyses from the micron to the atomic level at the NIMS Magnetic Materials Center made substantial contributions. Based on these results, high performance Dy-free neodymium magnets for hybrid vehicles, electric vehicles and wind generators are in progress.

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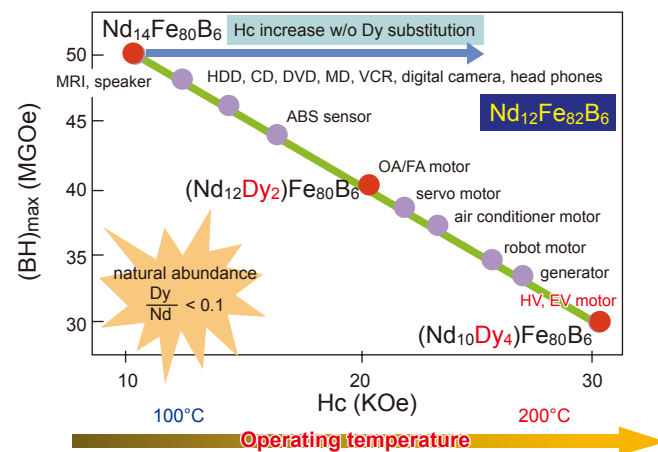
Fig.1 Maximum energy products and coercivity of commercially available neodmium sintered magnets. The typical compositions are included in the figure. When Nd is substituted with Dy, coercivity or heat resistance improves at the expense of the maximum energy product. If coercivity can be improved by controlling the microstructure without using Dy, the maximum energy product of 50 MGOe will be maintained even at higher coercivity.

[*] **heavy rare earth elements:** elements which are heavier (have higher atomic number) than Gd in lanthanide

Fig.2 Back scattered electron (BSE) scanning electron microscope (SEM) image of a sintered neodymium magnet. The magnet comprises a main phase of $Nd_2Fe_{14}B$ grains (gray) and a Nd-rich phase (white). Coercivity varies greatly depending on the composition and structure of the grain boundaries of the main phase and the interface between the Nd-rich phase and the main phase.

[**] **NEDO:** New Energy and Industrial Technology Development Organization
[***] **MEXT:** Ministry of Education, Culture Sports, Science and Technology

Phosphors Emitting Light Using Trace Amounts of Rare Earths

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A light source that makes efficient use of rare earths.

Phosphors are materials which emit light in response to external energy such as light, electrical fields, and electron beams, and are used in familiar products such as fluorescent lamps. In recent years, white light LEDs, which employ a combination of phosphors and LEDs, have been applied practically in light bulb-type LED lighting and backlights for liquid crystal displays. Popularization of these devices is progressing rapidly. In comparison with conventional fluorescent lamps, white light LEDs are an environment-friendly light source, as they are more energy efficiency and do not use mercury.

In phosphors, rare earths such as europium (Eu), cerium (Ce), and terbium (Tb) are used as the light emission center and play the role of emitting light. These rare earths are not the main constituent of the phosphor, which contains only trace amounts of these substances. The ratio of rare earths relative to the main constituent is extremely small, being around 0.1-0.3at%[*], and conversely, light emission efficiency is reduced if large amounts are added. These trace rare earths function efficiently as a light emission center.

In these white light LEDs, the amount of phosphors used can be greatly reduced because light is emitted from a microscopic region on the LED, unlike conventional fluorescent lamps, in which light is emitted from the surface (see **Fig. 1**). Moreover, because LEDs have a long service life, consumption of phosphors accompanying replacement of lighting devices is also reduced.

We are conducting research on phosphors which emit light efficiently even with trace amounts of rare earths, and are promoting development to a variety of new applications in addition to white light LEDs.

Looking at the rare earths in phosphors from the viewpoint of crystal structure.

Various methods are used to stabilize these rare earths in the crystal structure of the main constituent.

Fig. 2 shows the crystal structure of a substance called α-SiAlON, which is one example of a phosphor used in white light LEDs. The cage-shaped spatial positions shown by the orange polygons in the figure are occupied by calcium. Yellow, orange, and red light-emitting phosphors are realized by replacing a very small part of this calcium with europium, which serves as a light emission center.

In the structure called β-SiAlON, green light emission is realized by doping a very small amount of europium in a 1-dimensional channel space. This is a phosphor which has a narrow light emission line width and is suitable as a light source for use in backlights.
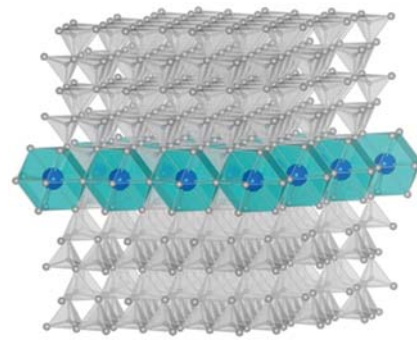
In aluminum nitride phosphors, a blue light phosphor is realized by inserting europium in a layered form in the crystal structure of the main constituent, as shown in **Fig. 3**. This phosphor has excellent characteristics when used with electron beam excitation.
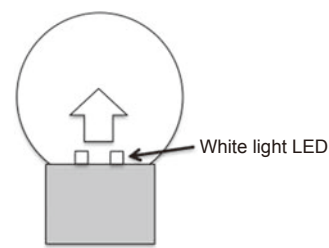
Thus, in phosphors, it is possible to realize light emission colors from blue to red and characteristics suitable for diverse applications such as white light LEDs, etc. by stabilizing trace amounts of rare earths in crystal structures by diverse methods. Our goal is to develop phosphors with even higher performance.

Fig.1 Schematic diagram of a white light LED. The amount of phosphors (rare earth elements) used can be reduced because light is emitted from a very small area.

White light LED

Fig.2 Diagram of the crystal structure of an α-SiAlON phosphor.

Fig.3 Diagram of the crystal structure of an aluminum nitride phosphor.

[*] **at%:** Means "atomic percentage"; a percentage determined by the relative numbers of atoms of different elements.
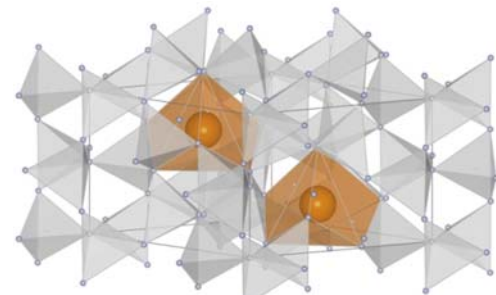
Development of Electrode Material for Fuel Cells Using Cerium Oxide (Ceria)

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Rare Earth and the Fuel Cell.

With international attention focused on strategic approaches to the use of rare earths, more careful study of the possibilities, related research and development, are demanded.

Cerium oxide, or ceria, has been an object of research as a material for use in solid oxide fuel cells (SOFCs). In previous work, we studied the effects of changes in the internal microstructure in ceria solid electrolytes and the microstructure at the interface between ceria solid electrolytes and ceria anodes on the properties of fuel cell devices, and have published a large number of new findings in papers in scientific journals.

On the other hand, the development of heated catalysts which utilize the oxygen storage/release capacity of ceria is also underway, centering on auto makers. We are engaged in research focusing on the possibilities of ceria as an oxide-type fuel cell material and catalyst material, and on the role of ceria as an electrode carrier material for polymer electrode fuel cells (PEFCs). This article presents recent results.

New Electrode with Cerium Oxide developed by NIMS.

In fuel cell electrodes, an anode and a cathode are necessary. The oxygen reduction reaction (ORR) proceeds on the cathode, and the reaction by which protons are formed from hydrogen proceeds on the anode. As the electrode reaction on the cathode proceeds through a complex route, this reaction is delayed. As a result, loss in the cathodic reaction is a serious problem. On the anode side, if the hydrogen contains even a trace amount of carbon monoxide (CO) of less than 5ppm, this CO will be strongly adsorbed on the platinum (Pt) surface, resulting in the problem of reduced anode properties.

To solve these problems, we fabricated a cathode and anode having an amorphous ceria interface with the Pt. **Fig. 1** shows the results of a fuel cell single-cell performance test (NIMS PtCeOₓ/CB) using the fabricated cathode and a commercial Pt anode. **Fig. 2** shows the results when a commercial Pt cathode and the NIMS-fabricated anode were used, together with the results of a fuel cell performance test with 5ppm CO contamination of the hydrogen.

In **Fig. 1**, a satisfactory current-potential curve was obtained in comparison with the case of using a commercial platinum cathode (Pt/CB). From **Fig. 2**, it can be understood that the decrease in cell potential resulting from CO contamination of the hydrogen was reduced when the Pt-ceria interface fabricated in this research was used.

In order to explain why these functions appeared when ceria electrodes were used, a study is being carried out using *in-situ* X-ray absorption fine structure analysis (XAFS) in the synchrotron radiation facility, and is gradually clarifying the reasons for these phenomena.
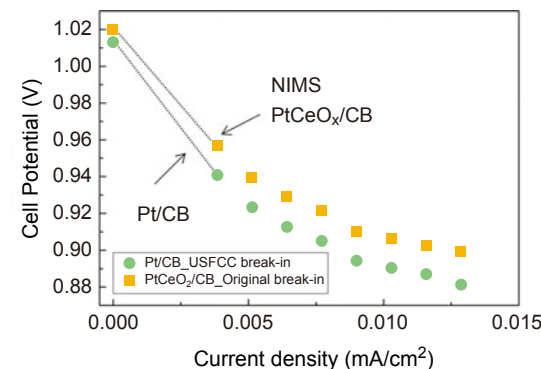
We have introduced new latent possibilities using ceria in this article as an example. We are engaged in ongoing research in the expectation that we can still discover many possibilities based on an better understanding of rare earth compounds.

Fig.1 Comparison of generating performance using a NIMS-developed Pt-ceria cathode and an commercial Pt cathode.

Fig.2 Comparison of fuel cell performance using (a) commercial Pt anode and (b) NIMS Pt-ceria anode (current: 800mA, operating temperature: 70°C, CO=5ppm).

Next-Generation Refrigeration "Magnetic Refrigeration" and the Rare Earths

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Recently, readers may have heard the term "magnetic refrigeration". Magnetic refrigeration is a refrigeration technology which uses a magnetic field and a magnetic substance, or refrigerant. Magnetic refrigeration does not require refrigerants with high environmental impacts and, in principle, efficiency is high. Based on these advantages, development of magnetic refrigeration as a key for next-generation room temperature refrigeration technology is currently underway worldwide.

Magnetic refrigeration was originally a technology for producing ultra-low temperatures below 0.1K, but the possibility of room temperature magnetic refrigeration is now being pursued in the field of refrigeration as one means of achieving technical innovation aiming at solid-state refrigeration, in much the same way that electronic devices evolved from gas (vacuum tube) to solid-state (semiconductor) technology.

Principle and problems of magnetic refrigeration.

The principle of magnetic refrigeration is shown in **Fig. 1**. In place of the conventional refrigeration cycle of compression and expansion of a gaseous refrigerant, magnetic refrigeration employs magnetization and demagnetization of a magnetic material. The basic principle is simple, in that heat is generated when the magnetic material is introduced into the magnetic field, and heat is absorbed when it is removed.

However, one serious difficulty arises when this operation is used in a refrigerator at room temperature, as a powerful magnetic field is necessary to realize the magnetocaloric effect of the magnetic material at room temperature. For example, in order to achieve the maximum magnetocaloric effect of Gd at room temperature, a gigantic magnetic field exceeding 200T (Tesla) is required. Because the practical magnetic fields which can be generated with permanent magnets are limited to a maximum of 1T, this is totally impractical.

Therefore, research and development on both magnetic materials and the refrigeration cycle is being carried out in order to overcome this difficulty.

Magnetic refrigeration and the rare earths.

Table 1 shows one example of representative magnetic materials. The most important condition in magnetic materials for use in magnetic refrigeration is large change in the magnetic entropy generated by the magnetic field. Conventionally, it had been thought that the large magnetic moment of the rare earth elements was effective. Because this change in the entropy of magnetic materials is based on a second order transition, a strong field is necessary. However, the development of magnetic materials which combine a first order transition and second order transition, which are termed structural transition and metamagnetic transition, has made it possible to generate large changes in entropy with weak fields. In **Table 1**, the Gd-Si-Ge, La-Fe-Si, and Fe-Mn based materials, etc. are materials of this type. Where the refrigeration cycle is concerned, the active magnetic regenerator (AMR) cycle has been proposed, and desktop-sized prototypes using permanent magnets have already appeared. Because these devices generate temperatures from sub-zero to more than 40°C, and refrigeration capacity has increased to several 100W, it is possible that this technology will enter the phase of full-scale popularization within the next 10 years.

However, rare earths are used in considerable quantities in magnetic refrigeration, and efforts to reduce dependence on these substances are indispensable. Fortunately, progress is being achieved in the development of Fe-Mn, La-Fe-Si, and other materials which are superior in terms of cost and availability, but use little or no rare earths. Likewise, in technologies for generating magnetic fields, it will be essential to end dependence on the rare earths by considering the use not only of permanent magnets, but also other magnets which employ new superconducting wiring materials.

NIMS is currently studying the development of magnetic refrigeration materials and systems which incorporate high temperature superconducting technologies and energy saving technologies based on the development of magnetic refrigeration technologies to date. By utilizing superconducting technology, which is one of the strengths of NIMS, it will be possible to realize higher efficiency with rare earths, enabling dramatically improved refrigeration performance, and to reach a new stage in magnetic refrigeration technology.

Takenori Numazawa Dr. Eng. Joined NRIM in 1984. Visiting Researcher at MIT's Francis Bitter Magnet Laboratory (FBML) in 1989. Appointed as Senior Researcher at NRIM in 1991, and was a NASA Visiting Researcher in 2001. Present position since 2001.

Fig.1 Principle of the magnetocaloric effect

Table 1 Representative examples of magnetic refrigeration materials.

name of material (= Abbreviation)	Magnetic transition temperature	Refrigeration cycle
CrK(SO$_4$)$_2$•12H$_2$O=CPA	0.009	Carnot
FeNH$_4$(SO$_4$)$_2$•12H$_2$O=FAA	0.026	Carnot
Gd$_3$Ga$_5$O$_{12}$=GGG	0.85*	Carnot
Dy$_3$Al$_5$O$_{12}$=DAG	2.4	Carnot
ErAl$_2$	12	AMR
GdPd	38	AMR
DyAl$_2$	63	AMR
GdNi$_2$	71	AMR
Gd$_5$Si$_{0.9}$Ge$_{3.1}$	120	AMR
Gd$_5$Si$_2$Ge$_2$	260	AMR
Gd	293	AMR
La(Fe$_x$Si$_{(1-x)}$)$_{13}$H$_y$	280	AMR
MnAs	315	AMR

Material Developments and Effects on the Global Environment from the Viewpoint of the Center for Strategic Natural Resources

Kohmei Halada
Managing Director,
Center for Strategic Natural Resources

Activities of the Center for Strategic Natural Resources.

The Center for Strategic Natural Resources arranges and analyzes information on the supply and circulation of resources which are indispensable for the development of materials, and on the accompanying environmental effects.

The representative work of the Center from the period of its predecessor, the Strategic Use of Elements Interdisciplinary Cluster, to the present are as follows.

1) "2050 Metal Consumption Forecast", which predicted that in 2050 the demand for many metals will be several times the present reserves.

2) "Estimation of Potential of Urban Mines in Japan", which showed that the potential of urban mines in Japan is comparable to that of the world's leading resource nations. (Urban mines: resources obtained by recycling minor metals from used electronic products, etc.)

3) "Japan's Basic Materials Industries from Viewpoint of Trade Flows", which showed that exports of industrial basic materials are a source of activity for Japan.

In addition to the above, the Center also analyzes the trade flows and material flows of a diverse range of metals and calculates the total material requirement (TMR), that is, the amount of all natural resources consumed in the extraction and refining of metals.

Investigating how rare earths are used.

Among these activities, examples of data related to the rare earths are presented here. **Fig. 1** shows the domestic material flow of rare earths. From **Fig. 1**, it can be understood that Japan uses a large amount of ceria abrasives, and the yield of Nd sintered magnets is around 60%, indicating that the significance of in-process recycling is large. From the rare earth trade flow, virtually 100% of these trade flows involve transactions with China

and Japan, Japan exports to Thailand, Malaysia, and other countries, and rare earths are also exported to Southeast Asian countries as processed basic materials after refining to higher purities in Japan.

Use of rare earths considering environmental impacts.

Although not limited to rare earths, calculation of TMR is important for understanding the environmental impact of materials. In the future, products must be designed and used based on a knowledge of their global environmental impacts in the extraction of natural resources. The NIMS Center for Strategic Natural Resources is the only organization which calculates TMR for all metals.

Fig. 2 shows CO_2 generated in the manufacturing of metals on the x-axis and TMR on the y-axis. The degree of cell toxicity is shown by the size of the bubbles. Although virtually no cell toxicity has been reported for the rare earths, the TRM of the rare earths follows that of the platinum group and precious metals, and CO_2 emissions also occupy a position similar to these materials. Therefore, as a direction for the use of rare earths, these facts show that highest priority should be given to efficiently realizing the properties of the rare earths.

In addition to these activities, the Center for Strategic Natural Resources has also organized various forums for discussion of the outlook for future technologies in cooperation with external experts ("bessemar+200, 2050 Workshop on the Future of Steel", "Workshop on New Extraction Technologies by Fusion of Nano/Organic/Metallurgical Techniques", "Workshop on Recycling of Rare Earth Magnets"). The Center is also involved in actual technical development related to recycling, for example, development of a crusher which enables instant disassembly of cell phones.
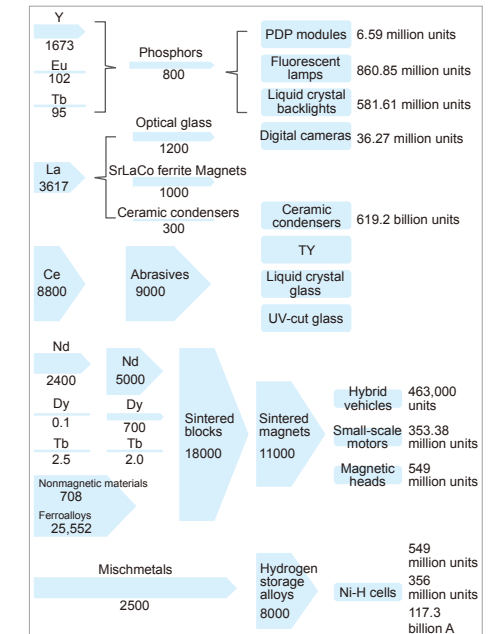

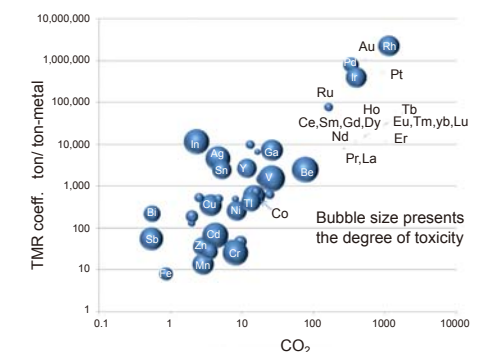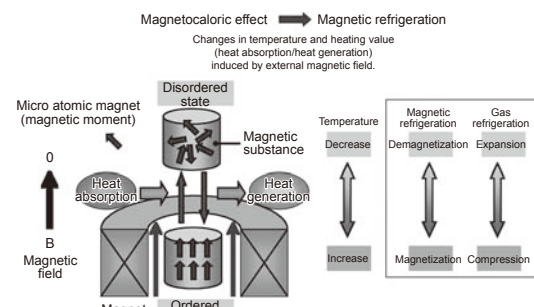**Fig.1** Material flow of rare earths in Japan (unit: ton).

Fig.2 Total material requirement (TMR) and cell toxicity.

Profile is on P3

High-Field Magneto-Spectroscopy in Carbon Nanotubes
First Observation of the Large Anisotropy of Magnetic Susceptibility in Metallic Carbon Nanotubes

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Yasutaka Imanaka
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Single-walled carbon nanotubes have a cylindrical structure, which is formed by rolling a single layer of graphite, i.e. graphene, into a tubular shape. It has been demonstrated, both theoretically and experimentally, that the electrical conductivity of CNT can be controlled to both metallic and semiconducting states through the chirality of the tube. As the conductivity of CNT can also be controlled by the magnetic field, it is quite essential to study the basic properties of CNT by using high magnetic fields.

In transport measurements of CNT, the fabrication of contacts is the most significant problem for carrying out measurements, in particular, under the restricted experimental conditions in the small bore of the high field magnet. Therefore, optical techniques are widely used for studying the basic properties of CNT as a contactless method. In high-field optical measurements under polarization, the preparation of aligned CNT samples is quite important, and mechanically-aligned CNT samples dispersed in a polymer were used in experiments. However, with samples of this type, there are always difficulties in realizing high orientation and obtaining qualitative data on the anisotropic properties of the CNT fixed on the polymer.

In the present research, we carried out linear polarized absorption measurements of self-aligned CNT in an aqueous solution under high magnetic fields up to 35T by using the Hybrid Magnet (a combined magnet comprising both a superconducting magnet and a resistive magnet) in NIMS. We also developed an optical fiber probe for the present measurements. This enables us to study the linear polarized measurements of CNT samples even in the small bore of the Hybrid Magnet, and the anisotropy of magnetic susceptibility can be extracted qualitatively from the linear dichroism.

Fig. 1 (top) shows the polarized absorption spectra in the CNT at B=35T. A large difference in absorption between the
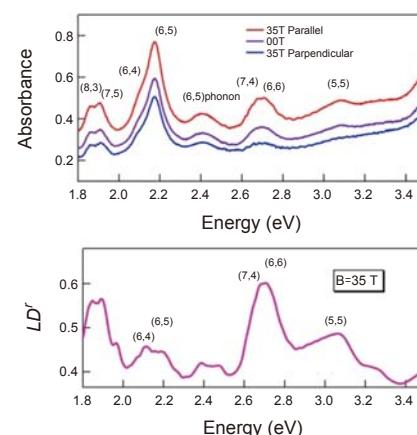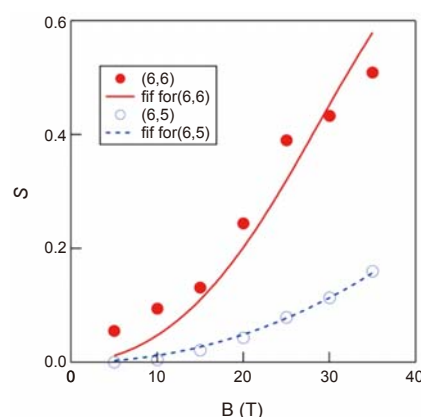

Fig.1 (top) Linear polarized absorption spectra (parallel and perpendicular to the CNT axis) at a high magnetic field (B=35T) and zero field, and (bottom) linear dichroism (LD^r) obtained from the difference of two polarized data in the top figure. The parentheses (n, m) at absorption peaks indicate the chirality of the CNT.

Fig.2 Magnetic field dependence of a representative metallic (red circles) and semiconductor (blue circles) carbon nanotubes, and theoretical fitting curves (red solid line and blue dashed line).

two configurations of the linear polarizer (parallel and perpendicular to the CNT axis) was observed. This is due to the self-alignment of the CNT in the high magnetic field resulting from its large anisotropy of magnetic susceptibility between the axial and radial directions.
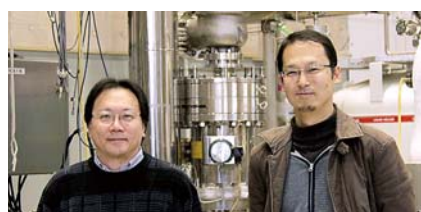
The linear dichroism (i.e., degree of alignment of the CNT) was calculated from the difference between the absorption data of the different polarizations, as shown in Fig. 1 (bottom), clarifying the considerable differences in the degree of alignment for tubes having different chirality.

The magnetic field dependence of the magnetic alignment up to B=35T is shown in **Fig. 2**. We have confirmed qualitatively that the anisotropy of susceptibility in the metallic CNT is 2-4 times greater than that in the semiconducting CNT in the present analyses.

We plan to continue magneto-absorption measurements in very high magnetic fields, in particular, with metallic-enriched CNT samples. Further detailed experiments on the metallic family of the CNT will be performed soon in NIMS.

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Thomas Searles Doctoral course student of the Department of Electrical and Computer Engineering, Rice University.

Reference literature: T. A. Searles, Y. Imanaka, T. Takamasu, H. Ajiki, J. A. Fagan, E. K. Hobbie and J. Kono; Phys. Rev. Lett., 105, 017403 (2010).

Dense Array of Nanometer-Scale Light Sources on a Large Area Substrate
Toward Application to High Efficiency Sensors

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Near-field light[(i)] is a key nanotechnology which enables high resolution beyond the diffraction limit and therefore is the principle of the near-field optical microscope, whose resolution reached 50nm. Conventionally, nanometer-scale point light sources have been the megatrend in the use of this technology, as nanofabrication and microscope technologies which were conscious of achieving high resolution beyond the diffraction limit made remarkable progress.

As another aspect of near-field light, because it is possible to collect light, application to optical sensors, photovoltaic cells, and similar fields has been expected in recent years. However, due to the inefficient optical power of one point light source, practical large-area plane light sources with sizes of cm^2 to m^2, which are typical sizes of devices in these fields, are necessary to realize these devices.

In the present work, we have succeeded in fabrication of a large-area near-field light source by densely arraying gold (Au) nanoparticles (NPs), which are point light sources (near-field light), on an Au-plated quartz substrate with an area of 1cm^2 (**Fig. 1**). Concretely, we focused on the aggregation phenomenon of colloidal AuNPs coated with alkanethiol molecules which form arrays by self-assembly. On the basis of self-assembly, the group succeeded in developing a large-area near-field light source that is densely constructed (coverage>95%) of uniform-size AuNPs two-dimensionally arrayed with regular interparticle gaps, which has tunable localized surface plasmon resonance bands 600-1100nm of AuNPs using a hybrid synthesis method combining the two techniques described below. The first technique, electrophoresis, guides AuNPs onto a conductive substrate. The second, solvent evaporation, gives a supersaturated condition at the liquid surface to nucleate AuNP two-dimensional (2D) arrays on the conductive substrate. It is also possible to realize mechanical strength of the AuNP 2D array, which has chemical bonding between the AuNPs and the conductive substrate,
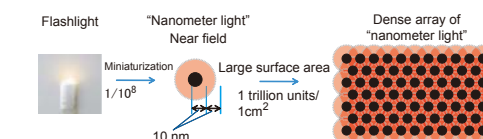
Fig.1 Schematic illustration of near-field light. When 1 trillion units of a point source of "near-field light," which is nanometer scale light reduced to 1/10^8 the size of ordinary light, are arrayed on an substrate with a size of 1cm^2, nanometer scale light is arranged over the entire 1cm^2 surface.
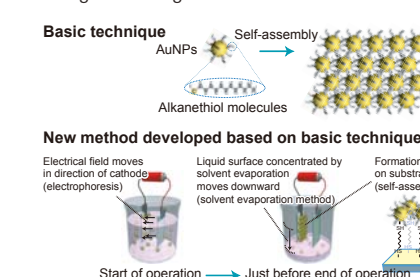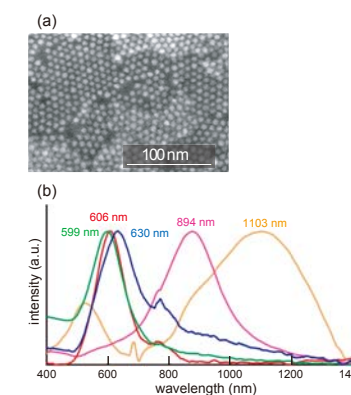

Fig.2 Schematic illustration of method arraying AuNPs. (Top) Base technology, self-assembly on substrate and (bottom) Developed method based on base technique.

Fig.3 (a) SEM image and (b) optical absorption spectrum of 2D arrays of AuNPs. The wavelength of the near-field light can be coarse-adjusted by changing the size of the AuNPs and fine-adjusted by changing the length of the alkanethiol.

through the terminal thiol groups of alkanedithiol molecules coating the surface of the conductive substrate (**Fig. 2**).
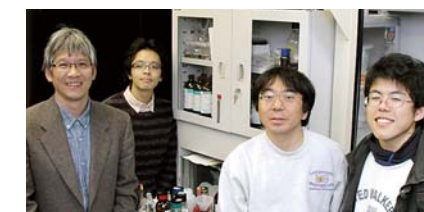
Fig. 3(a) shows a scanning electron microscope image of 2D arrays of AuNPs with diameters of 10nm. It is not necessary that the 2D array on the substrate be a single crystal, but is sufficient that it be a polycrystal with a regular interval and order up to about 3rd-4th neighbors.

The wavelength of the near-field light source is tunable from 600nm to 1100nm, that is, the wavelength can be controlled from the visible light region to the near infrared region by modifying the size of the AuNPs and the distance between the adjoining particles (**Fig. 3(b)**).

Until now, application of near-field light has been limited to scientific fields. By proposing and demonstrating a new synthesis method which makes it possible to form a large area near-field light source from point light sources, as described above, this research opens the way to application of near-field light to various practical technologies, such as high-sensitivity optical sensors and high-efficiency solar cells.

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Takao Ochiai (right) M.Eng. Currently enrolled in the Doctoral Program in Materials Science and Engineering (D1), Graduate School of Pure and Applied Sciences, University of Tsukuba. NIMS Junior Fellow.
Tomoya Taguchi (second to left) M.Eng. Currently enrolled in the Doctoral Program in Materials Science and Engineering (D2), Graduate School of Pure and Applied Sciences, University of Tsukuba. JSPS Research Fellow (DC2).
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NEWS NIMS Exhibits at the APEC JAPAN Exhibition.

NIMS participated in an APEC JAPAN Exhibition, "Japan Experience: Ideas into Reality", which was held in conjunction with the Japan APEC Leaders' Week from Nov. 6 to 14 (venue: Pacifico Yokohama Exhibition Hall).

The themes of this exhibition were "Regional economic integration", "Strategies for growth", and "Human safety and security", which were also the three main issues of Japan APEC. The exhibition was a demonstration of Japan's world-leading technologies and various initiatives.

Under the title of "Advanced Material Technologies for Solving Environmental and Energy Problems", NIMS exhibited 1) Super heat resisting alloy turbine blade and gas turbine model, 2) SiAlON phosphors, and 3) Visible light-responsive photocatalysts. The NIMS exhibit received a large number of visits from groups representing the 21 countries and regions of APEC, as well as members of the media.

SiAlON phosphors and visible light photocatalysts.

Super heat resisting alloy turbine blade and gas turbine model.

NEWS NIMS New Partnership

On Oct. 23, Dr. Hisatoshi Kobayashi, Group Leader of the Biofunctional Materials Group, Biomaterials Center, NIMS, visited the University of Allahabad in India, and signed a memorandum of understanding (MOU) between the NIMS Biomaterials Center and the Nanotechnology Application Centre (NAC) of the University of Allahabad.

The University of Allahabad is one of India's oldest leading universities, having been established in 1887, and is known for its central role in India's liberation movement.

Based on this agreement, they plan to activate exchanges of researchers and students in the future, aiming at joint research and development of nanomaterial-based sensors, bioimaging, regenerative medicine, and medical devices.

Following the signing ceremony, Dr. Kobayashi received the title of Adjunct Professor of the University of Allahabad's Nanotechnology Application Centre.

From the left, Prof. Pandey of the University of Allahabad, Professor Srivastava, Vice-chancellor of University of Allahabad, Dr. Kobayashi, and Dr. Ashutosh Tiwari (NIMS JSPS Fellow).

Hello from NIMS

Vaishali Shinde (India)
ICYS Researcher
Since Oct 2008

From my school days I know Japan as the land of rising sun and the Japanese miracle of economy. My teacher always advised us to visit Japan at least once in life to experience the perfection and devotion. And I got that dream opportunity when I was invited for interview of the position of ICYS Researcher and later when I was selected for the same post. During my stay as ICYS since last two years, I have enjoyed the excellent international atmosphere, superior scientific opportunities with perfect research facilities. Although, the life here is different from India the kindness, helping and caring nature of Japanese people make it easier, rather pleasant. NIMS maintain a good balance between professional activities and personal life in Japanese culture by arranging

[With my husband at Mt. Bandai]

occasionally fascinating Culture class. As a part of it, I attended language classes and could learn some basic Japanese at NIMS which is very useful for communicating in daily life. Besides, I have attended and enjoyed most of the cultural classes organized by NIMS, such as Ikebana flower arrangements, Kimono event, Edo-Komon printing workshop, Japanese acupuncture and Karate class, and very recently Wadaiko drum class and looking forward for future cultural classes too.

On weekends we often go for hiking with TWMC (Tsukuba Walking and Mountaineering Club) group and explore the seasonal diversity and splendor with charming and murmuring beauty of mountains and greenery. The hiking usually ends up with soaking ourselves in Onsen (hot spring) which all together gives relaxation and energy to get back to work. Recently we visited Mt. Bandai which is erupted mountain and famous for 'Five Colored Lakes'. I am very looking forward for continuing research as well as exploring Japan especially hiking on Mt. Fuji.

And finally, I am thankful to NIMS for giving me such an opportunity.

[Moments at different cultural classes.]