NIMS NOW

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RESEARCH FRONTLINE

Nanoscale oxygen generators: MgO_2 fillings of BN nanotubes

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Utilising nanotubes (NTs) as ultimate ultra-light gas containers has attracted major interest with respect to practical applications. Hydrogen and nitrogen were observed to penetrate, remain inside and be easily released from C NTs. However, the possibility of using NTs as localised oxygen burners and/or generators has not yet been investigated. In addition, gaseous oxygen is expected to quickly damage the interior of a C NT structure via fast oxidation at relatively moderate temperatures (~400-600℃), making a C NT-based oxygen container probably unfeasible. A BN NT is the counterpart of a C NT in which alternating B and N atoms entirely substitute for C atoms in a honeycomb network.

There were two objectives in this research: (i) BN NTs are much more stable in terms of oxidation in air, than C NTs; (ii) compared to other peroxides, MgO_2 can steadily generate O_2 over a long period of time.

Therefore we prepared open-ended BN NTs, only tens nanometers in diameter, filled with an oxygen-release MgO_2-based compound which easily decomposes inside the NTs and thus locally generates oxygen when subjected to marginal heating (up to ~90 ℃), *e.g.* by an electron beam, and/or just during room temperature aging. Thus the first nanoscale oxygen burner or generator was created.

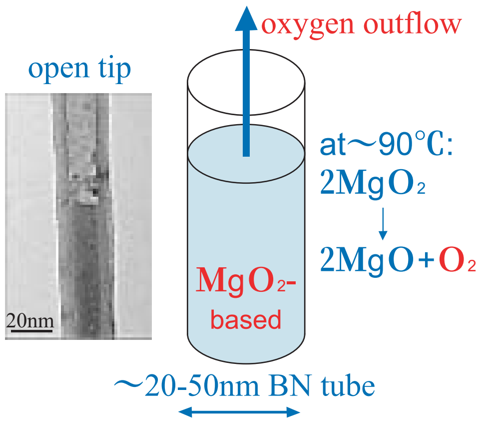

Fig. HRTEM image of a MgO_2-filled BN NT heated by an electron beam of the microscope (left); and a sketch of oxygen outflow from the tube (right). Note melting of the filling, appearance of voids in it (bright contrast dots) and its fragmentation to many sharp-edged cubic MgO fragments as a result of oxygen escape through the open-tube-end.

A mixture of B and MgO (molar ratio 1:1) was placed in a BN crucible and heated to 1300℃ in a high-frequency induction furnace. At this temperature B reacted with MgO to form B_2O_2 and Mg vapors. The vapors were transported with the aid of an Ar flow into a reaction chamber whose temperature was set to ~1550℃, with subsequent introduction of a flow of NH_3. A BN material crystallized on a Mo substrate located in the upper zone of the chamber through a simple chemical reaction between B_2O_2 and NH_3.

Figure depicts a MgO_2 -filled BN NT and a sketch of oxygen outflow from it on marginal heating.

Several intriguing practical applications of the observed phenomenon are anticipated. Localized (several tens of *nm* pipe cross-section) O_2 outflow may selectively and effectively produce nanosize metallic domain oxidation. This may be applied in quantum dots preparation or local insulation of parts of a given conducting network composed of inorganic conducting nanowires. Study on various biological cell, bacteria, and/or individual molecule interaction with a point (nanometer size) oxygen source may shed light on their living and deteriorating conditions. This may be of high value in biological and medical science.

In this issue

NIMS NEWS

Agreement on Joint Graduate School System with Leading Australian Universities

On August 7, NIMS concluded an agreement with five Australian national universities (Sydney, Melbourne, New South Wales, Queensland, and Western Australia) based on a system of international cooperation among graduate schools in the field of material science.

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Development of Solid-state NMR by High Magnetic Fields

—From protein analysis to next-generation catalysts and a quantum computer—

Tadashi Shimizu
Magnetic Field Applications Group
High Magnetic Field Center

NMR (nuclear magnetic resonance) magnets, including MRI, account for approximately 90% of the ¥100 billion market for superconducting materials and play a central role in both superconductor and magnetic field applications. Because the accuracy of NMR improves as the strength of the magnetic field increases, high-intensity magnetization is a universal development element for NMR (see figure). In the 1960s, chemical analysis became possible when superconducting magnets replaced electromagnets, and in the 1980s, the appearance of 10T (Tesla) class superconducting magnets (500 MHz) enabled structural analysis of proteins. Now, in the 2000s, we are seeing the start of the new analytical field of inorganic solid material NMR using a 920 MHz (21.6T) superconducting magnet developed by the High Magnetic Field Center.

In principle, NMR can be used to analyze more than 90% of the elements in the periodic chart, but because measurement accuracy is low in conventional magnetic fields, analysis had been limited to the easily-observed main 4 nuclides, such as hydrogen, etc. As a result, NMR was popularized as a specialized analytical device for organic substances. However, in magnetic fields of 20T and over, accurate measurement of metallic elements, oxygen, etc. also becomes possible, enabling NMR analysis of solid materials, which play critical roles in numerous applications.

A distinctive feature of NMR, in comparison with other microscopic analysis technologies such as the electron microscope and synchrotron radiation , is the fact that the local atomic position, electron structure (type and strength of chemical bond, role of electron spin) and other properties can be detected with pinpoint accuracy. We believe that this feature has the following possibilities.

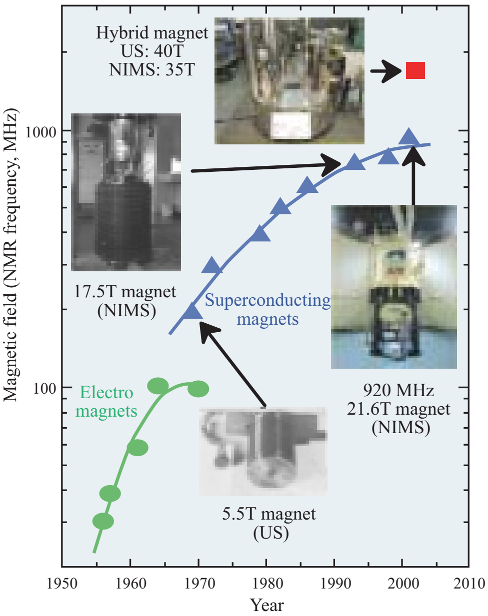

Fig. Progress in NMR magnets.

1. Acquisition of design guidelines for the development of catalysts with higher performance than existing materials by designating the position, type, and strength of the chemical bond between the catalyst and reacting molecules.
2. Elucidation of the coordination state and low-symmetry local structure of designated elements, and reflection in solid electrolytes for fuel cells, oxygen separation membranes, and similar technologies, and improvement of the properties of functional inorganic materials such as super-hard materials and heat-resistant materials.
3. Elucidation of the mechanism of superconductivity and establishment of guiding principles for searching for new superconductors.
4. Elucidation of super-polarization phenomena in semiconductors (nuclear magnetization and NMR signal intensity increase by maximum of five figures), and application to advanced fields such as biotechnology and quantum computers.

High magnetic field NMR is now a worldwide trend, and the advanced countries have already begun development of NMR in fields of 30T and higher. We fortunately possess a 40T class hybrid magnet and intend to press ahead rapidly with the technical development of NMR measurement using this device in cooperation with the private sector and universities

17.3 T Achieved with Conduction-Cooled Magnet using 2K

The Cryogenics Group succeeded in generating a high magnetic field of 17.3 T, which is a world record for a conduction-cooled magnet.

Conventional superconducting magnets are cooled with liquid helium. Recently, however, a number of magnets with improved stability have been developed by impregnation with epoxy etc. and do not necessarily require immersion cooling with liquid helium. Rather, these magnets can be used with simple and convenient conduction cooling with a refrigerator. With the development of the Gifford-McMahon (GM) refrigerator, the conduction-cooled magnet technology has developed rapidly. Recently, magnets exceeding 12 T are commercially available. The highest magnetic field in a conduction-cooled magnet to date was 15.1 T, which was achieved with a 4K GM refrigerator manufactured by Sumitomo Heavy Industries, Ltd. in 1998.

With existing technologies, it has been considered difficult to realize higher magnetic fields than those mentioned above, and particularly fields exceeding 18 T, without improving superconducting properties by decreasing the temperature

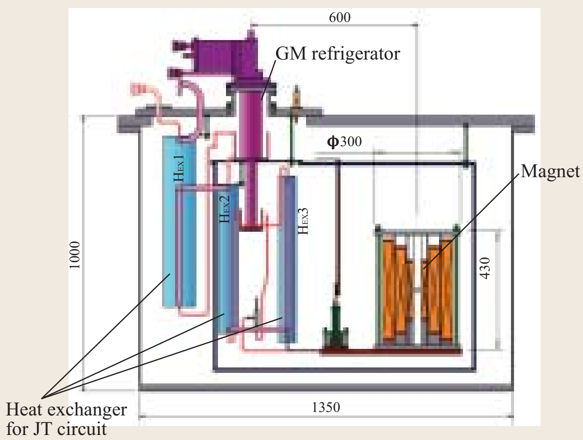

Fig.1 Internal structure of 2K cooled magnet (unit: mm).

920 MHz NMR Spectrometer

—Ultra-high resolution measurement of proteins realized through joint research with RIKEN —

Hideaki Maeda
(NIMS guest researcher)
The Institute of Physical and Chemical Research (RIKEN)

Tsukasa Kiyoshi
Magnet Development Group
High Magnetic Field Center

The High Magnetic Field Center developed a 920 MHz (21.6T) magnet, which features the world's highest magnetic field in a persistent operation, and applied this device to a spectrometer for structural analysis of proteins in a joint project with the Institute of Physical and Chemical Research (RIKEN) and JOEL, Ltd. The completed NMR spectrometer enables triple resonance measurement from hydrogen, carbon, and nitrogen nuclei.

An example of measurement with this spectrometer is shown in the figure. The measured protein (DEF-C/ICAD) has the function of contributing to cutting DNA in the final stage of apoptosis (cell death). The method of nitrogen nucleus edited NOESY is used in NMR measurements. NOESY is an extremely important measurement technique for structure determination, providing information on the distance between pairs of hydrogen atoms. As shown in the figure, measurement results are dramatically different at 500 MHz (11.75T) and 920 MHz, as three times as many individual signals can be obtained at 920 MHz. This means to shorten the measurement and to improve accuracy for structural analysis.

To date, the object proteins for NMR have been limited to those with relatively low molecular weights (20,000 to 30,000). However, Prof. Wüthrich, the 2002 Nobel Prize laureate in chemistry, developed a pulse sequence called TROSY which makes it possible to measure proteins with higher molecular weights. Because TROSY is most effective with magnetic fields around 1 GHz (23.5T), the developed NMR spectrometer is suitable for this technique. When actual TROSY measurements of large protein composites such as DNA bound proteins and membrane proteins were performed, it was possible to obtain signals which were extremely sharp and strong in comparison with those of conventional devices.

In the "National Project on Protein Structural and Functional Analyses," which is currently underway in Japan under the leadership of RIKEN, structural/functional analyses of 3000 representative proteins are to be performed using NMR and other techniques. We are confident that the development of an NMR spectrometer with the world's highest sensitivity and resolution will make an important contribution to progress in research on structural and functional analysis of proteins in Japan.

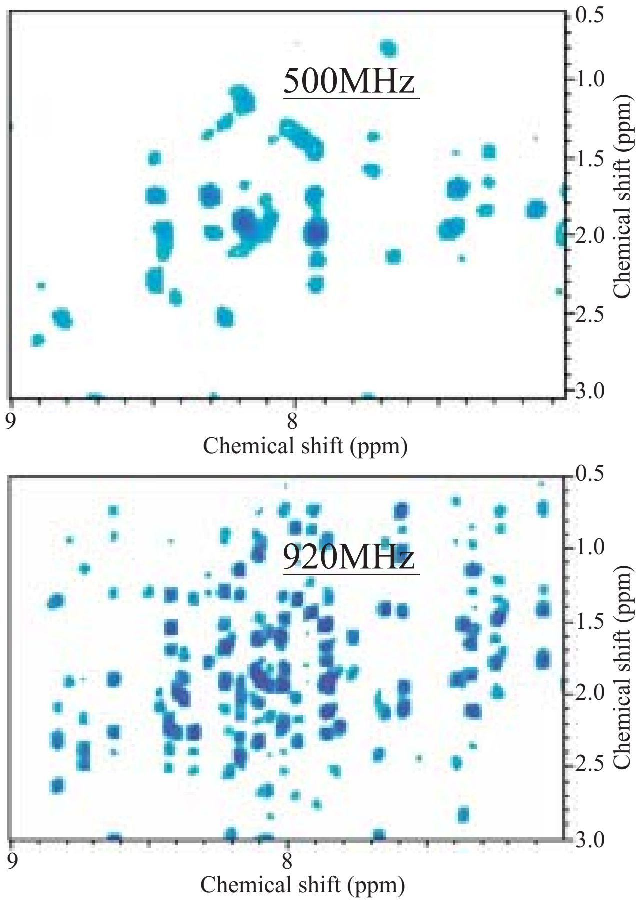

Fig. Examples of NOESY spectra of proteins at 500 MHz and 920 MHz Chemical shift.

Refrigerator

Akio Sato
Cryogenics Group
High Magnetic Field Center

Fig.2 Appearance of 2K cooled magnet.

to 2K or under. However, with the GM refrigerators, the refrigeration capacity at 2K is only a very slight several tens of milliwatts, while magnet cooling requires at least 1 W or higher.

The Cryogenics Group developed a 2K refrigerator for application to conduction-cooled high- field superconducting magnets and other cryocooler applications. This is a GM type refrigerator which combines a Joule-Thomson (JT) expansion circuit and GM-JT refrigerator (Fig. 1, 2). A low pressure-drop heat exchanger was developed, and a two-stage design was adopted for the JT expansion circuit to optimize performance, improving the refrigeration capacity to the 1 W class at 1.8 K, which is necessary for magnet refrigeration.

A small-scale magnet was manufactured to demonstrate that the device can be applied to high- field magnets. The dimensions of the magnet were outer diameter, 254 mm, height, 350 mm, and innermost diameter, 30 mm. The magnet consisted of three coils. The outer magnet was made with NbTi wire, while the two inner magnets were made with Nb_3Sn wire. When cooled to 2 K, a large current could be passed in the superconducting condition, in comparison with 4 K cooling. Thus, the device is extremely compact for a 17 T class magnet.

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High Magnetic Fields and Molecular Devices

—Artificial light-harvesting antenna created by self-assembled porphyrin rings—

Ken Takazawa
Magnetic Field Applications Group
High Magnetic Field Center

Photosynthesis is the process by which plants and bacteria convert sunlight into the energy necessary for life. Recent research has gradually elucidated the mechanism of photosynthesis. For example, in photosynthesizing bacteria, tiny nanometer-size rings play the role of light-collecting "antennas."

These antennas consist of a regular, ring-shaped arrangement of porphyrin molecules. When an antenna receives light, the light energy travels along the ring at high speed to a "power plant", which generates electric energy. The antenna absorbs light efficiently and transmits energy to the power plant with virtually no loss, enabling photosynthesis to produce energy more efficiently than any solar cell.

The Magnetic Field Applications Group discovered the possibility of artificially synthesizing the light-harvesting antennas of the natural world by the method called self-assembly. When a newly-synthesized porphyrin derivative molecule (hexakis porphyrinato benzene) was dripped on a substrate and the solvent was evaporated, ring-shaped molecular aggregates were formed by self- assembly. Moreover, by changing the substrate surface treatment, the size of the rings can be controlled as desired within a range from nanometers to micrometers.

Figure 1 shows fluorescence images of rings measured with a laser. The horizontal and vertical fluorescence intensity of the rings changes depending on the polarizing direction of the exciting light, showing that the molecules in the rings have a regular arrangement (Fig. 2). Interaction between molecules in a ring is required for movement of energy along the ring. Analysis of fluorescence from the rings revealed a strong molecular interaction, suggesting a high possibility that these rings have a light-harvesting antenna function.

A detailed investigation of energy transfer along these rings at cryogenic temperatures and in high-intensity magnetic fields is now in progress. We believe that energy transfer can be accelerated by applying a high-intensity magnetic field. If so, dramatic improvement in the antenna function will be possible.

(This research began as a joint project with the Physics Dept. and Chemistry Dept. of University of Nijmegen in the Netherlands.)

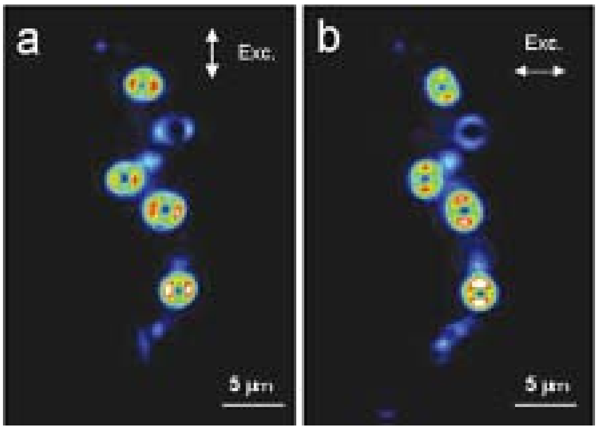
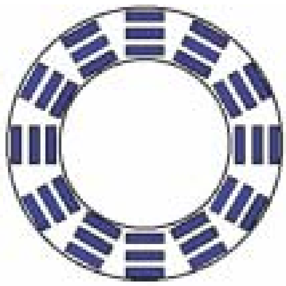


Fig.1 Fluorescence image of rings with a) vertical and b) horizontal polarizing excitation.



Porphyrin derivative molecule

Fig.2 Schematic diagram of molecular arrangement within ring.

7th Workshop on Ultra Steel

A workshop called "Ultra Steel: Requirements from New Design of Construction" was held at the Tsukuba International Congress Center on June 23-24. As one important feature, this meeting provided a forum where researchers and engineers from the user and manufacturer sides could discuss common issues and share information and perceptions under the motto "Materials are of value only when they are really used." The conference included 51 presentations at a total of 11 oral presentation sessions such as "Proposals and Tasks for New Steel Structures Utilizing Ultra Steels" and "Welding and Joining Technologies for Realizing High-Strength/High-Performance Structures," and allowed an energetic exchange of ideas among researchers and engineers from civil engineering/construction and the automotive industry. In addition, a poster session featuring 116 items gave participants a broad understanding of recent developments in technology transfer of ultra steel research project results.

As one unfortunate note, a group of researchers from China was unable to participate. However, Dr. H. Dong of the Central Iron and Steel Institute (CISRI), who was the scheduled keynote speaker, sent his presentation materials in advance. These were read in his place, allowing those present to hear his most recent research results. We would like to express our deep appreciation to all of the Chinese delegates who had planned to participate, and particularly to Dr. Dong.

Among many highlights, we were particularly impressed by the words of Prof. D. Senk of the Aachen University, who reminded us that "Steel means Future. Metallurgy is One of the Keys." With this in mind, the Steel Research Center is steadily progressing with the project "How to use from how to make." We wish to thank all of the 411 persons who participated in this conference for their enthusiastic support.

Magnetic Chromatography

—Aiming for secondary waste free chemical analyzer applicable to radioactive waste analysis—

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Magnetic Field Applications Group
High Magnetic Field Center

Kazunari Mitsuhashi
Graduate School of Pure and Applied Sciences
University of Tsukuba

Everyone knows that iron sand and steel objects such as nails are attracted to magnets, but can a magnet also attract metal ions floating in an aqueous solution? We proved experimentally that this is possible.

This is an extremely significant finding, as it verified the principle of a new analytic method called magnetic chromatography. Because techniques, which use of easily- demagnetized magnetic force eliminate the need for the bonding/chemical combination with solids or liquids required with conventional analytical methods, they do not produce residual chemical byproducts. This feature is particularly advantageous when analyzing radioactive substances, where secondary waste is a serious problem.

The superconducting magnet shown in Photo 1 was used as the magnet. To generate a strong magnetic force (magnetic field gradient), a metal magnetic column was introduced into the bore of a dipole-superconducting magnet. While applying a magnetic field, an aqueous solution containing transition element cations was passed through the column, and the cation flow was measured with a detector. Cation retention time increased in comparison with the case where no magnetic field was applied, indicating that the flow of cations was retarded by magnetic force in the magnetic column. Experiments were conducted with ions of iodine (diamagnetic) and four types of transition metal elements (paramagnetic) using various ion concentrations and magnetic field intensities. The ion retention time changed in each case.

Figure 2 shows an example of measurement of the cobalt ion Co^{2+}. The ordinate is the ion concentration in the aqueous solution after passing through the column, and the abscissa is time. Ions required more time to pass through the magnetic column as the strength of the magnetic field applied on the column was increased. This was attributed to the stronger magnetic force retarding the ion flow. However, to check for possible problems in the reliability of observation results due to the effect of the magnetic field on the measuring instrument, an experiment was conducted with iodine ions, which have extremely low magnetic susceptibility. In this case, no differences were observed in the waveform, as shown in the figure, regardless of the intensity of the magnetic field.

These results demonstrated that ions can be identified by length of retention time that depends on magnitude of magnetic susceptibility, thus clearly demonstrating the possibility of magnetic chromatography, which uses magnetic force as its basic principle. With further development, an analytic device, which utilizes clean magnetic force, can be realized.

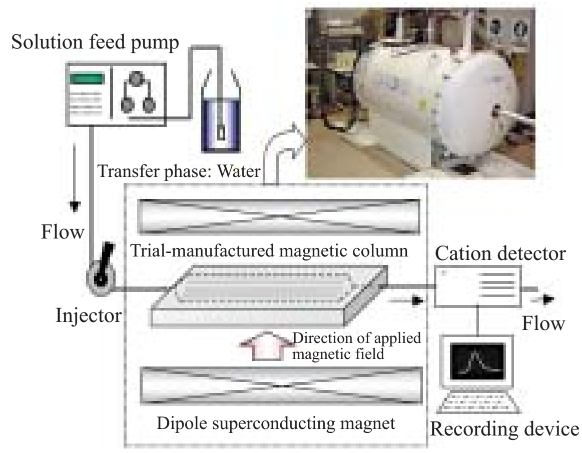
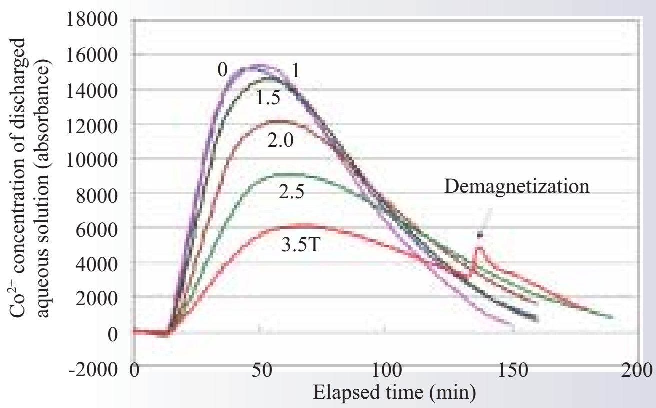


Fig.1 Device used to verify action of magnetic force on metal ions.



Experimental condition
Sample: 3.8 mol/L aqueous solution of $CoCl_2$
Amount introduced: 20 μL, mobile phase: water,
flow rate: 0.3 mL/min, detection wavelength: 516 nm

Fig.2 Dependence of flow retard of cations on magnetic force.

NIMS NEWS

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Agreement on Joint Graduate School System with Leading Australian Universities

This agreement, which will promote close cooperation with the five main national universities in Australia, is the first attempt by a Japanese institution to create a cooperative graduate school system simultaneously with multiple foreign universities, and will enable more efficient implementation of research education activities.

In addition to developing human resources, NIMS expects this agreement to give impetus to its mission of building a research base with its doors open to the world.

PRESS RELEASE

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17.3 T Achieved with Conduction-Cooled Magnet using 2K Refrigerator

The development of 2K refrigerator cooling technologies is expected to enable unattended operation using small refrigerators, even with NMR magnets which have required supply of liquid helium to date, and other high magnetic field magnets exceeding 20 T. Moreover, adoption of the 2K refrigerator will also allow more compact design of magnets of 15 T and under, and as a result, progressively lower costs can be expected.

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