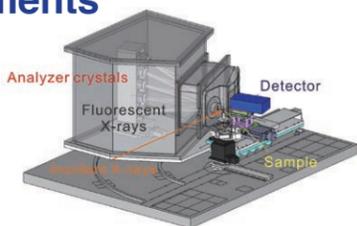


### Observing Hidden Electronic States of Trace Elements

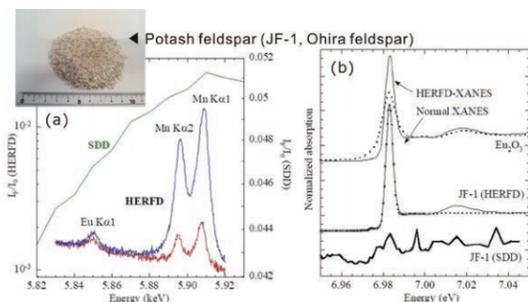
Rare-earth elements are used in various highly functional materials. Recently, the exploration and recovery of natural resources containing rare-earth elements have become important issues. Analytical techniques for elements contained in natural minerals are limited, especially when those elements are present in trace amounts. For example, the direct detection of the electronic state of europium (Eu) in natural samples has been impossible by conventional techniques because the Eu content of a crustal material is generally 1 mg/kg or less. Such a detection limit is determined not by Eu concentration but by the superposition with high fluorescence emissions from manganese (Mn) contained in the same natural samples. The separation of the fluorescence emission of Mn from that of Eu is therefore necessary to determine the electronic state of Eu.

X-ray emission spectroscopy (Fig. 1) is a technique for observing fluorescent X-rays with a high energy resolution. Using this technique, it is possible to extract the fluorescent X-rays from trace elements that could not be observed using a semiconductor detector capable of energy-dispersive analysis that is used for conventional fluorescent X-ray analyses. Also, with its high energy resolution, X-ray emission spectroscopy provides a spectral structure that is clearer than the conventional X-ray absorption near-edge structure (XANES), enabling the detailed observation of electronic states. In this study, issues with conventional XANES measurements were resolved using X-ray emission spectroscopy. The Eu valence in a common rock-forming mineral, potash feldspar, with a Eu concentration of 5 ppm or lower was determined by high-energy resolution fluorescence detection (HERFD)-XANES measurement. The sample used here was JF-1, a standard rock issued by Geological Survey of Japan (GSJ), prepared from natural feldspar (Ohira feldspar) in Nagiso, Nagano, Japan (Fig. 2).

**BL39XU** Rimi Konagaya, Yoshio Takahashi (The University of Tokyo)  
Article: R. Konagaya *et al.*, *Chem. Lett.* **50**, 1570 (2021)



**Fig. 1** Schematic diagram of X-ray emission spectrometer. The fluorescent X-rays from the sample are dispersed and focused with a high energy resolution using an analyzer crystal. Their intensity is measured using the detector.



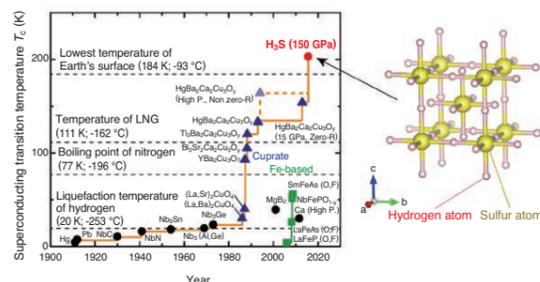
**Fig. 2** (a) Fluorescent X-ray spectra of JF-1 sample obtained using semiconductor detector (SDD) and X-ray emission spectroscopy (HERFD). (b) XANES spectra of JF-1 sample obtained using SDD and HERFD.

### Clarifying Crystal Structure of Sulfur Hydride Exhibiting High-Temperature Superconductivity under Ultrahigh Pressure

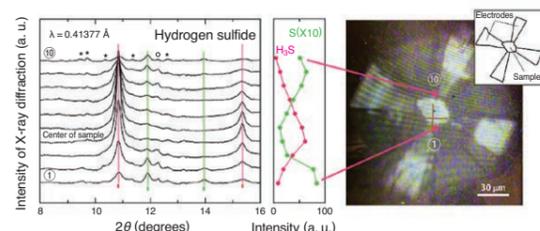
Some materials do not exhibit superconductivity at ambient pressure but become superconductors under high pressure. Among those materials, hydrogen and hydrogen-rich compounds have for many years been expected to become room-temperature superconductors under ultrahigh pressure. Recently, hydrogen sulfide (H<sub>2</sub>S) has been found to have a superconducting transition temperature  $T_c$  of -73°C under an ultrahigh pressure of 150 GPa. Such a  $T_c$  value eclipsed the previous highest  $T_c$  of a copper-oxide superconductor, HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> (Fig. 1▲), by more than 30°C and exceeded the lowest temperature on Earth's surface (-93°C). Hydrogen sulfide is a pioneering hydrogen-rich compound, which exhibits high-temperature superconductivity under high pressure. However, its crystal structure, which is important for understanding the mechanism of its superconductivity, has remained unknown. In this study, the crystal structure of the high- $T_c$  phase was investigated by the simultaneous measurements of powder X-ray diffraction and electrical resistance in a pressure range of 110–190 GPa and a temperature range from room temperature to -263°C at the high-pressure research beamline BL10XU in SPring-8. Hydrogen sulfide is composed of light elements, sulfur and hydrogen, and the sample is very small (less than 30 μm in diameter) and thin for ultrahigh-pressure generation. Therefore, the high-luminosity and high-energy (30 keV) X-ray focused on a half bandwidth of 2 μm available at BL10XU is very effective for analyzing the distribution of a microscale sample in a pressure-generating device called a diamond anvil cell (Fig. 2). In this study, it was clarified for the first time in the world that the high- $T_c$  phase is H<sub>3</sub>S with sulfur atoms arranged in a body-centered cubic structure (Fig. 1, right) and that hydrogen sulfide, H<sub>2</sub>S, molecularly dissociates into H<sub>3</sub>S and sulfur under high pressure.

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**BL10XU** Mari Einaga (Osaka University)



**Fig. 1** (Left) Temporal evolution of the superconducting transition temperature  $T_c$  and (right) predicted crystal structure of the high-temperature superconducting phase (high- $T_c$  phase) of H<sub>2</sub>S.



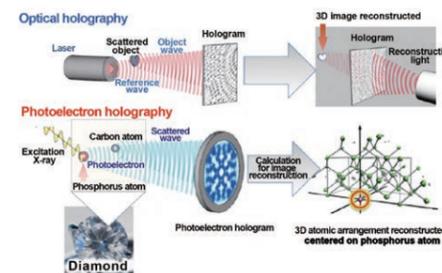
**Fig. 2** (Left) Sample distribution in a pressure device obtained by X-ray scanning and (right) the microscopic image of the vicinity of the sample at 150 GPa. The result of this scanning indicates that there is a large amount of H<sub>3</sub>S near the center of the sample.

### Clarifying 3D Atomic Arrangement of Dopant in Diamond

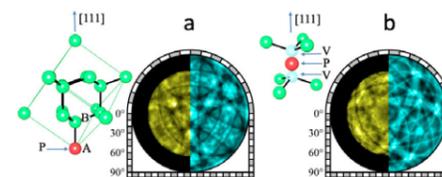
Diamond is an important material not only for its beauty as a gem but also for its excellent properties such as high hardness, high thermal conductivity, and good insulating performance. Diamond is attracting attention from the perspective of element strategy in Japan, a resource-limited country, because it is a crystal of carbon, a common element. Diamond, with its good insulating performance, is a promising material for realizing next-generation power devices and quantum sensors because it becomes a high-performance semiconductor when doped with small amounts of other elements. For device applications, it is necessary to introduce electrons or holes (electron vacancies) into diamond by doping to make it conductive. p-type semiconductors can be synthesized by boron doping, whereas n-type semiconductors can be synthesized by phosphorus doping. Improvements in the quality of those semiconductors will be an important factor that determines device performance.

In this study, ultrahigh-precision photoelectron holography was performed on a phosphorus-doped n-type diamond film (phosphorus concentration: 0.06 at.%; provided by Dr. Hiromitsu Kato of AIST) fabricated by chemical vapor deposition (Fig. 1). The 3D atomic arrangement of elemental phosphorus in diamond, which could not be observed by conventional techniques such as electron microscopy and X-ray crystal structure analysis, was clarified for the first time in the world. Doped phosphorus atoms are incorporated into diamond in the following two structures: (a) a structure where a carbon atom of diamond is substituted by a phosphorus atom (lattice substitution) and (b) a structure where two adjacent carbon atoms are removed and a phosphorus atom is located between two carbon-atom sites. Whereas (a) is an electrically active structure emitting electrons in the diamond crystal, (b) is an inactive structure capturing electrons. It was also observed that (b) is a structure oriented in the diamond growth direction. The atomic arrangement of phosphorus and the electrical activation state in diamond were thus “visualized”. Advanced strategies for sample preparation, such as increasing the concentration of the active structure while suppressing the inactive structure, can be developed by changing the crystal growth conditions of diamond and observing the changes in its structure during measurements.

**BL25SU** Takayoshi Yokoya (Okayama University), Tomohiro Matsushita (Nara Institute of Science and Technology)  
Article: T. Yokoya *et al.*, *Nano Letters* **19**, 5915 (2019)



**Fig. 1** Conceptual diagram of photoelectron holography.



**Fig. 2** Photoelectron hologram and reconstructed atomic arrangement of phosphorus in diamond.

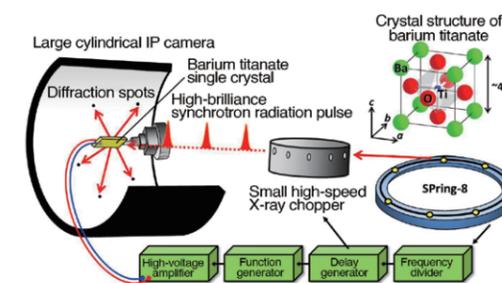
### Capturing atomic movement of millionths of a second

Piezoelectric crystals contract and deform macroscopically upon the application of an electric field. This phenomenon was discovered by J. Curie and P. Curie in the late 19th century. Nowadays, piezoelectric devices based on this phenomenon are used in various applications such as the control of ink ejection of printers and the touch panels of cell phones; thus, piezoelectric devices are indispensable in our daily lives. Although various mechanisms behind the significant deformation of the exterior of piezoelectrics have been discussed, the process from voltage application to the displacement of atoms in the crystal at the micron level should be examined to understand the fundamentals of the mechanism. However, this atomic displacement is extremely small and difficult to detect. Therefore, even the movement of crystal lattices has remained unclarified thus far.

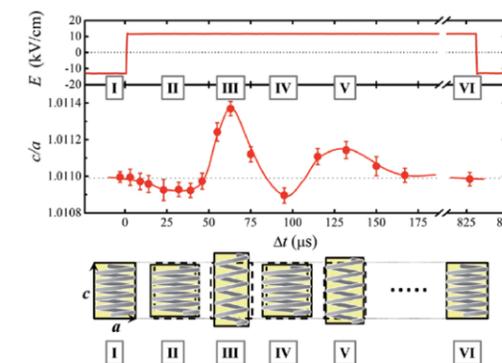
In this study, the research group succeeded, for the first time in the world, in the in situ observation of the time-course change in the lattice of a piezoelectric crystal that underwent piezoelectric vibration on the order of microseconds. This was achieved by combining two advanced measurement techniques: precision crystallography and high-speed time-resolved measurement at SPring-8 BL02B1 (Fig. 1). The research group is the first ever to observe that an expanded crystal lattice, owing to the application of an electric field, deformed as if it were a spring undergoing damped vibration (Fig. 2). In addition, we observed an interesting phenomenon that the crystal lattice contracted once during the polarization reversal that occurred immediately before the crystal lattice greatly expanded.

The above achievements are expected to promote research on the nano- or picosecond-order dynamics of atomic displacement and to enable the “fluoroscopic” observation of the behavior of the atoms in working electronic devices. Moreover, the measurement techniques used in this study can be applied to the development of new materials for electric storage devices such as capacitors and batteries.

**BL02B1** Chikako Moriyoshi, Yoshihiro Kuroiwa (Hiroshima University)



**Fig. 1** Time-resolved X-ray diffraction experiment using synchrotron radiation pulses at SPring-8



**Fig. 2** Dynamic response of piezoelectric crystal to applied voltage