Laser performance of J-KAREN-P facility laser

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The J-KAREN laser facility [1] delivered a single-shot on-target intensity of 10¹⁷ W/cm² with a temporal contrast of ~10¹³. J-KAREN has been upgraded to J-KAREN-P to realize petawatt (PW) peak-power pulses on target at a repetition rate of 0.1 Hz with an intensity capability of over 10²² W/cm². Such progress in high-field science will give rise to new applications and breakthroughs, including relativistic particle acceleration, bright X-ray source generation, and nuclear activation. Many other interesting features can be investigated with PW and higher-intensity laser pulses, including relativistic transparency and radiation friction.

J-KAREN-P is shown schematically in Fig. 1. The output pulses with high temporal contrast and uniform spatialprofile from the power amplifier [1] are up-collimated and enter booster amplifier 1 (BA1), which uses an 80-mm-diameter Ti:sapphire crystal pumped with ~50 J from two commercial Nd:glass green lasers at a repetition rate of 0.1 Hz. The pulses from BA1 are then amplified in booster amplifier 2 (BA2), which uses a 120-mm-diameter Ti:sapphire crystal pumped with ~100 J from four commercial Nd:glass green lasers at 0.1 Hz. A deformable mirror is installed in the laser chain to correct the wavefront distortion. The amplified pulses are up-collimated to a diameter of ~250 mm, and finally, compressed in the compressor consisting of four 1,480 grooves/mm gold-coated gratings of 565 × 360 mm².

A maximum output energy of 23 J was achieved with an incident pump energy of 47 J, with a conversion efficiency of 49% from BA1. The near-field beam profile has a homogeneous and uniform spatial intensity distribution. The amplified spectrum from the Ti:sapphire amplifiers is red-shifted because of saturation. As a mitigating measure, the amplifier input spectrum is blue-shifted by tuning the phase-match setting of the BBO crystals in the OPCPA amplifier.

Figure 2 shows the measured dependence of the output broadband energy from BA2 on the total pump energy at a repetition rate of 0.1 Hz. A maximum output energy of 63 J is achieved with an incident energy of 92 J. The figure clearly shows that the experimental data fit the simulation. Figure 3 shows the typical spatial profile of the laser beam from BA2. The profile has a homogeneous and uniform intensity distribution (Fig. 3(a)).

After BA2, the wavefront distortions are corrected using a deformable mirror. The beam is then sent into the pulse compressor. The measured spectrum has a bandwidth of ~50 nm (FWHM). The recompressed pulse duration is obtained as less than 30 fs. The peak power is expected to be over PW at 0.1 Hz on target because the beam-line throughput from the laser room to the target chamber including the compressor is ~60%. With an f/1.3 off-axis parabolic mirror, according to measurements of the focal spot and encircled energy, a peak intensity of 10²² W/cm² is achievable with a power level of 0.3 PW [2] (Fig. 3(a)). The contrast is measured with a third-order cross correlator for the laser pulse without pumping the booster amplifiers, as shown in Fig. 4. The contrast earlier than 200 ps before the main pulse is 3 × 10⁻¹² (detection limited). At 100, 50, 10, and 5 ps before the main pulse, the contrast is roughly 10⁻¹¹, 6 × 10⁻¹⁰, and 8 × 10⁻⁹, respectively.

Laser-driven acceleration via the interaction of short, intense laser pulses with matter is known as laser-plasma acceleration. Compared to radio-frequency accelerators, it features higher accelerating electric fields, shorter acceleration distances, and shorter bunch lengths. Laser acceleration of protons [3] and electrons with the J-KAREN-P laser system is being tested. Currently, protons in excess of 50 MeV [4] are obtained with ~10²¹ W/cm² and GeV-class electrons are obtained with ~10²⁰ W/cm². We will optimize the target and increase the laser intensity gradually while checking the total system. Laser-plasma acceleration can replace the front end of a conventional accelerator system and would help greatly in downsizing accelerator systems, especially for heavy ions [5]. Also, in progress are experiments on (i) high-order harmonics from relativistic singularities [6,7], (ii) multi-MeV pure proton beam generation from micro-size hydrogen cluster targets [8], and (iii) X-ray spectroscopy of laser-plasma interaction in the ultra-relativistic regime [9].

From national laboratories to university departments, ultra-high-intensity lasers have evolved to become one of the most important scientific tools for studying matter in extreme states. The J-KAREN-P laser system is a leading facility in the provision and application of ultra-high-intensity lasers for the broad scientific community. It has been used in various pioneering and cutting-edge studies, which has resulted in high-impact discoveries for high-field science.

Multi-PW lasers are now being constructed for specific applications in many fields ranging from proton therapy for cancer treatment to the simulation of astrophysical phenomena. The next generation of lasers will approach exawatt (EW = 10¹⁸ W).
power levels and may allow us to reach conditions beyond those that occur naturally in the universe.

Acknowledgments

References
J-KAREN-P laser approached the diffraction-limited, bandwidth-limited Petawatt

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J-KAREN-P is a high-power laser facility aiming at the highest beam quality and irradiance for performing state-of-the-art experiments at the frontier of modern science. Here, we approached the physical limits of the beam quality—diffraction limit of the focal spot and bandwidth limit of the pulse shape—removing the chromatic aberration, angular chirp, wavefront, and spectral phase distortions. We performed accurate measurements of the spot and peak fluence after an f/1.3 off-axis parabolic mirror under full amplification at a power of 0.3 PW attenuated with 10 high-quality wedges, resulting in a Strehl ratio of ~0.5 and an irradiance of ~10^22 W/cm^2, which is the highest accurately estimated irradiance demonstrated to date.

The performance of ultrafast petawatt-class lasers has gradually and steadily improved in recent years. However, the final beam diameter of high-power lasers is typically 20–30 cm to prevent the damage caused to the compressor gratings. Such a wide beam makes it challenging to achieve a tightly focused beam with clean pulse compression. The major difficulties include wavefront and spectral phase distortions and various spatiotemporal couplings, e.g., chromatic aberration and angular chirp. If not dealt with carefully, all these effects result in poor focal spot and pulse shape, i.e., low irradiance. Typically, the irradiance drops by order(s) of magnitude, destroying the main advantage of high-power lasers, i.e., their high irradiance capability.

Importantly, we have measured the focal spot after an f/1.3 off-axis parabolic mirror (OAP) during 0.3 PW operation. The laser beam was attenuated by 10 wedges with high surface quality confirmed with interferometry. The resulting focal spot had a Strehl ratio of 0.46 ± 0.06 and an effective radius [3] r_{eff} = 1.02 ± 0.07 μm (Fig. 1). We have thus achieved the highest accurately characterized at-focus irradiance of 0.93(±0.12) × 10^22 W/cm^2.

We also performed a full-beam duration measurement, down-collimating the Ø280 mm beam to a few millimeters using a telescope consisting of two off-axis parabolic mirrors. The full-beam pulse duration and shape were nearly identical to the duration and shape measured using a few-millimeter-diameter pick-off, confirming the high spatiotemporal quality of the beam and the absence of spatiotemporal couplings.

This breakthrough was made possible by significantly improved laser performance [1] and careful design and accurate construction of the beamline (Fig. 3), including increased optics size, mirror-based low-aberration expanders, several monitors for reproducible alignment, a deformable mirror and wavefront sensors for wavefront correction (Fig. 4), attenuation paths, and focal spot monitors for accurate spot characterization.

The high quality of the J-KAREN-P laser will result in enhanced proton and ion acceleration, coherent x-ray generation, and electron acceleration in the on-going and near-future experiments.
Acknowledgments

This work was supported by MEXT (Supplemental budget, C-PhoST), JSPS (KAKENHI JP 26707031, 26247100, 16K05506), JST (PRESTO 960212), and the ImPACT Program. We thank the J-KAREN-P team, K. Sekiguchi, A. Kon, R. Rungsawang, I. Stefanon, and M. A. Alkhimova for their contributions, and H. Daido, D. Neely, C. G. R. Geddes, J. Fuchs, T. Zh. Esirkepov, J. Koga, A. Ya. Faenov, T. A. Pikuz, A. A. Soloviev, I. W. Choi, S. K. Lee, and X. Levecq for discussions.

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3. The effective radius is defined as $r_{\text{eff}} = \frac{\pi}{4} \frac{\int F(x,y) \, dx \, dy}{F(x,y)}$, where $F(x,y)$ is the normalized fluence distribution. The peak irradiance is $I_0 = \frac{P_0}{\pi r_{\text{eff}}^2}$; this estimate is correct, unlike the commonly used incorrect estimate of $P_0 / \text{FWHM}^2$.

4. The effective pulse width is $\tau_{\text{eff}} = \int t(t) \, dt$, where $p(t)$ is the normalized laser power. The peak power is $P_0 = \frac{E_\text{laser}}{\tau_{\text{eff}}}$; this estimate is correct, unlike the commonly used incorrect estimate of $E_\text{laser} / \text{FWHM}$. 

Fig. 3. J-KAREN-P beamline (part after the final amplifier is shown); the beamline is covered to reduce air fluctuations. M1–M7: monitors (far, near fields through dielectric mirrors). DM: deformable mirror. W1, W5, W6: wavefront sensors. P: periscope. ×1.5 and ×2.1: mirror expanders. [1–4]: alignment CCDs. OAP5–OAP7: high-quality $f = 2,000 \text{ mm}$ OAPs for alignment and beam characterization. OAP8: in-vacuum $f = 350 \text{ mm}$ ($f/1.3, 45^\circ$ deviation) OAP focusing the beam on target. T1 and T2: two target areas. S1–S8: focal spot monitors.

Fig. 4. J-KAREN-P wavefront; the values are rms errors. (a) Before deformable mirror, beam Ø90 mm. (b) After deformable mirror, beam Ø90 mm. (c) Before the compressor; the Ø280 mm beam is focused by the $f/7$ alignment OAP.
Delbrück Scattering with Polarized Gamma Rays to Probe Vacuum Polarization

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Probably the most common use of polarized light is when people go to see 3D movies at movie theaters. Images with a slight offset are shown on the movie screen with different polarizations. If viewed with the naked eye, all one sees is a blurred image. However, by wearing glasses that have different polarization-filter orientations for each eye, one can see a 3D image from a 2D movie screen. Similarly, we have found that by using polarized gamma rays when scattering them off atoms, we can "see" more clearly the nature of vacuum than would be possible with unpolarized gamma rays [1]. Vacuum can be polarized by electromagnetic fields by the formation of virtual electron–positron pairs [2]. The polarization effect of these virtual electron–positron pairs on electromagnetic waves is extremely small and difficult to detect. One way in which such an effect has been measured is by the scattering of gamma rays off the Coulomb field of atomic nuclei, which is called Delbrück scattering (Fig. 1), in which virtual electron–positron pairs that result from the interaction scatter the gamma rays [3]. The scattering cross section of Delbrück scattering increases as \( Z^2 \alpha^4 \) [2], where \( Z \) is the atomic number of the nucleus and \( \alpha \) is the fine-structure constant \( (\alpha \approx 1.6 \times 10^{-13}) \) [4]. Although this cross section increases rapidly with the atomic number, its isolated measurement is difficult. First, the elastic scattering of gamma rays from atoms is a coherent combination of four different processes, namely Rayleigh, Thomson, giant dipole resonance (GDR), and Delbrück scattering [5–7]. Second, unpolarized gamma-ray sources were previously used to measure it [5,6]. As a result, although scattering measurements have been performed for gamma rays of various energies, Delbrück scattering was measured on the basis that it is a necessary contribution to the total scattering for the results to agree with theoretical calculations [8]. In 1977, De Tollis and Pistoni pointed out that by using photons with polarization parallel to the scattering plane, two of the four scattering contributions, namely Rayleigh and GDR scattering, go to zero at scattering angles of 90° [9]. Now, high-flux linearly polarized gamma-ray sources from laser Compton scattering are becoming available, such as ELI-NP-GBS [10]. As a result, we investigated whether Delbrück scattering can be isolated using such polarized gamma-ray sources.

Thomson and GDR scattering amplitudes can be calculated fairly simply [11], but Rayleigh and Delbrück scattering amplitudes require more complex calculations. Rayleigh scattering amplitudes have been calculated previously using the relativistic second-order S matrix and form factors [12] and can be found in a database [13]. However, because we required finer resolution, we used the "ENTING" code to recalculate them [11,12]. Delbrück scattering amplitudes have also been calculated previously using the lowest-order vacuum polarization tensor, and exist in tabular form [14]. Because finer resolution was necessary and no code was available to calculate the Delbrück scattering amplitudes, we constructed our own code using the compact formulae from [9,15,16]. The values were found to agree with the tabular values. Because equations for the higher-order forms of Delbrück scattering are yet to be calculated, we chose regimes in which these effects are predicted to be small [8,17]. As a result, we calculated the amplitudes for 1,100 keV gamma rays scattering off tin (\( Z = 50 \)). Figure 2 shows the results of the calculations for the differential scattering amplitude for all four elastic scattering processes (reproduced from Fig. 4 of [1]). It can be seen that at \( \theta \approx 70° \), Delbrück scattering is much larger than that of the other three components, indicating that a measurement at this angle gives a nearly isolated measurement of Delbrück scattering [1].

In conclusion, we have found through extensive calculations that Delbrück scattering can be nearly isolated from other processes contributing to the elastic scattering of gamma rays from atoms. A precise measurement of this vacuum contribution to the scattering of gamma rays can lead to the discovery of new physics if the measurements disagree with theoretical models. In the future, experimental measurements are expected to be carried out at facilities with high-flux polarized gamma-ray sources.

Fig. 1. \( \gamma \)-ray scattering off Coulomb field of nucleus using the compact formulae from [9,15,16]. The values were found to agree with the tabular values. Because equations for the higher-order forms of Delbrück scattering are yet to be calculated, we chose regimes in which these effects are predicted to be small [8,17]. As a result, we calculated the amplitudes for 1,100 keV gamma rays scattering off tin (\( Z = 50 \)). Figure 2 shows the results of the calculations for the differential scattering amplitude for all four elastic scattering processes (reproduced from Fig. 4 of [1]). It can be seen that at \( \theta \approx 70° \), Delbrück scattering is much larger than that of the other three components, indicating that a measurement at this angle gives a nearly isolated measurement of Delbrück scattering [1].

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Fig. 2. Differential scattering amplitude verses angle for Delbrück scattering (D) and Rayleigh, Thomson, and giant dipole resonance scattering (R+T+GDR) at 1,100 keV for tin (reproduced from Fig. 4 of [1]).
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We have recently demonstrated experimentally the phenomenon of burst intensification by singularity emitting radiation (Fig. 1), where extremely bright coherent X-rays are emitted by relativistic density singularities in plasma driven by high-power ultrashort pulse lasers [1–3]. Promising scalings indicate that this compact ultra-bright coherent X-ray source can approach the brightness of present-day free electron lasers at photon energies from 10 eV to a few kiloelectronvolts. Coherent X-ray sources are indispensable in fundamental research and applications in life sciences, material sciences, and nanotechnology. Recent trends in development of coherent X-ray sources include two broad classes: large-scale accelerator-based X-ray FELs (XFELs) and compact laser-based sources such as X-ray lasers and atomic high-order harmonics. Fundamental limitations of conventional techniques severely hinder the development of a bright compact coherent X-ray source, especially at kiloelectronvolt photon energies. Relativistic laser plasma gives a new class of bright coherent sources. Among them, a substantial portion is based on the KPSI scientists’ inventions, which include relativistic high-order harmonic generation in overdense plasmas, e.g., via the relativistic oscillating mirror [4] or relativistic sliding mirror [5–6] model. Another important representative is based on coherent X-ray generation in underdense plasmas via the relativistic flying mirror [7–10] model.

BISER is a new phenomenon in which relativistic plasma singularities are used to obtain ultra-bright coherent X-rays. Our research combines several fields: catastrophe theory (i.e., the study of singularities), nonlinear plasma physics, and the development of coherent X-ray sources. Since the 1970s, it has been realized that structurally stable singularities play a fundamental role in nature [11]. Singularities explain a wide range of phenomena ranging from physical effects to animal behavior and social processes. For example, catastrophe theory explains the large-scale structure of the Universe (galaxy clustering) [12,13]. Singularities are produced widely by multi-stream flows, which are ubiquitous in nature, such as with shock waves and jets in astrophysical and laboratory plasmas. Catastrophe theory explains the existence, universality, and structural stability of singularities, i.e., their insensitivity to perturbations. If a singularity occurs in an emitting medium, the emission from the singularity location can be extremely intense and coherent because of constructive wave interference (N^2 effect) (Fig. 1). This is a fundamental general effect that is applicable to any medium capable of emitting traveling waves, e.g., electromagnetic, acoustic, or gravitational. However, this effect was overlooked for at least 40 years. We found indications of this effect several years ago [1,2]. We discovered experimentally a new surprising ultra-bright coherent X-ray source in relativistic laser plasma and developed a theory showing that the coherent X-rays are generated by relativistic plasma singularities. In particular, for linearly polarized lasers, the theory predicts two singularities situated in the laser polarization plane. In our recent paper [3], we confirmed this cornerstone prediction by demonstrating experimentally a nanometer-scale double source with individual emitters situated along the laser polarization (Figs. 2 and 3). This helped us finally to formulate the BISER mechanism and generalize it to other types of travelling waves, thereby eliminating the 40-year lacuna in knowledge.
Fig. 2. PIC simulation revealing X-ray sources at the electron density spikes (singularities), and an image of the two point-like sources obtained experimentally in the LiF plate.

Fig. 3. (a) Harmonic combs corresponding to the two point-like X-ray sources. (b) Detail of the spectrum. (c) Pulse train seen in PIC simulation. (d) Black: a portion of the pulse train from (c); red: transform-limited shortest-possible pulse deduced from (a).

Essentially, the singularity is a phase object through which elementary emitters flow continuously. This differs fundamentally from a compact bunch, which consists of the same emitters. Furthermore, in contrast to a particle bunch, the singularity is determined by the multi-stream flow and has a non-local nature. BISER radiation is both spatially and temporally coherent, as evidenced by the fringes in the LiF image and spectra in Figs. 2b and 3b, respectively. We emphasize that the spatial coherence of our point-like source is not explained by the propagation effect (van Cittert-Zernike theorem), which would require ~20 km propagation. Our source demonstrates coherence at a distance of 286 mm. Therefore, the fringes that appear in the image are due to source coherence and not propagation. This differs fundamentally from a typical phase-contrast experiment with an incoherent source.

Besides studying singularities in general, we showed that BISER is a promising coherent X-ray source. It is driven by relatively compact lasers (~10–50 m scale) focused on high-repetition-rate, debris-free gas-jet targets. Typical laser parameters are a pulse duration of 50–50 fs, a peak power of 2 TW to 1 PW, and a relativistic irradiance far greater than 1018 W/cm². BISER is favorably scalable, with a photon yield proportional to the laser power squared, which we demonstrated to be up to 120 TW [1,2]. Together with high photon numbers (we demonstrated 1010 photons/pulse in the 60–100 eV spectral range) and extremely small source size (tens of nanometers), BISER exhibits a very high peak spectral brightness, e.g., 1021 photons/mm²·mrad²·s in 0.1% bandwidth. This is much brighter than any synchrotron, although two-to-three orders of magnitude lower than that provided by the brightest available sources, namely FELs. However, unlike present FELs, BISER is not only spatially but also temporally coherent, ultrashort (simulations show ~100 attoseconds), and compact, and available for university and industry laboratories.

Acknowledgments
We thank the J-KAREN laser operation group. We acknowledge financial support from JSPS KAKENHI JP 25287103, 25390135, and 26707031 and from the European Regional Development Fund (High Field Initiative, CZ.02.1.01/0.0/0.0/15_003/0000449).

References
Development of a proton beam profile diagnostic for laser-plasma ion sources

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The interaction of a high-intensity laser with a plasma is an attractive source of ion beams because of their high peak current, high charge, and low emittance and because of the compactness of the accelerator [1]. During the laser interaction with thin foil targets, electrons are heated to relativistic energies and form a sheath at the target surface. This sheath can accelerate surface ions to high energies. Typically, protons are accelerated preferentially because of their high concentration in surface contaminants and high charge-to-mass ratio.

Experiments conducted over the last few decades have primarily been performed at low repetition rate, motivating the use of passive single-use diagnostics such as radiochromic film stacks or nuclear track detectors. However, state-of-the-art Ti:sapphire lasers have recently demonstrated ~1 Hz repetition rates with the peak power and energy required to generate >MeV ion beams [2]. This has motivated the need for a new class of high-repetition diagnostics, particularly for transverse beam profile measurements, for which the transverse beam pattern depends on the energy band of the typical thermal spectrum.

Recently, plastic scintillators have been used to perform proton-beam profile measurements from laser plasma accelerators. They are attractive because of their flexibility, large size, and modest cost, as well as not being sensitive to the copious electromagnetic noise generated during the laser-plasma interaction. Preliminary studies showed measurement of multi-MeV proton beams with good spatial resolution but poor energy resolution [3]. A variation of the technique was recently demonstrated, in which differential filtering was used to form macro-pixels of different energy bands, sacrificing spatial resolution for significantly improved energy resolution [4]. However, in those initial studies, little attention was paid to scintillator nonlinear response and calibration.

We have therefore developed a simple and robust novel scintillator-based proton-beam profile (SB-PBP) diagnostic based on differential filtering, providing a flexible compromise between spatial and energy resolution [5]. We consider the nonlinear scintillation response and use accurate calibration to provide a true estimate of the angularly resolved energy spectrum. We also show that this technique can be used for protons in excess of 20 MeV, significantly higher than that demonstrated previously.

The response of plastic scintillators to ion irradiation is well known to be nonlinear with stopping power dE/dx because of ionization quenching [6]. Typically, the semi-empirical Birks model is used to characterize this, in which the density-normalized scintillation yield \( L^{\eta} = L / \rho \), in units of total energy of emitted photons per unit path length per incident particle, is given as

\[
\frac{dL^{\eta}}{dx} = \frac{dE}{dx} \frac{\eta}{1 + kB \left( \frac{dL^{\eta}}{dx} + C \frac{dL^{\eta}}{dx} \right)^2},
\]

where \( kB \) and \( C \) are experimentally determined scintillator-dependent constants and \( \eta \) is the scintillation efficiency. In this study, we used the EJ-232Q-0.5% scintillator and \( kB \) and \( B \) from recent calibration data of the chemically identical BC-422Q [7], and calibrated \( \eta \) using a known dose of 80 MeV protons at the Hyogo Ion Beam Medical Center (HIBMC), Japan.

We calculated the expected photon yield of incident protons of different energies entering the scintillator after passing through differential filtering (here, PTFE of differing thickness) by performing a series of TRIM [8] Monte Carlo simulations. The stopping power in the scintillator was taken from the simulations, and Eq. (1) was then integrated to calculate the scintillator yield. The total luminescence as a function of incident proton energy is shown in Fig. 1a. Increasing the thickness of the filter removes the contribution from lower-energy protons. Therefore, by using differing filter thickness and making an assumption about the incident energy spectrum of the protons, it is possible to reproduce the absolute original spectrum approximately.

In the design that follows, we use a macropixel with four different thicknesses (Fig. 1b and c), with each pixel 5 × 5 mm². This is performed by interlacing bars of differing thickness (or material, if desired) in a square lattice, making it easy and cheap to fabricate. Laser proton sources feature diverging beams; therefore, the angular resolution of the beam profile depends on the macropixel size and the distance between the target and detector. The energy resolution depends on the number of thicknesses used. It is simple to change this and the macropixel size, thereby optimizing the trade-off between spatial and energy resolution for each experimental setup.

We tested the diagnostic on an ion-acceleration experimental campaign with the J-KAREN-P laser at the Kansai Photon Science Institute, National Institutes for Quantum and Radiological Science and Technology, Japan. A \( \sim 15 \, \text{J}, \sim 40 \, \text{fs} \) pulse was focused with an f/1.3 off-axis parabola onto a thin foil target at a 45° angle of incidence. Proton beams in excess of \( \sim 30 \, \text{MeV} \) were generated. To benchmark the SR-PBP diagnostic, we sampled the upper half of the proton beam as shown in Fig. 2.

![Fig. 1.](image-url)

- a) Total scintillator luminescence as a function of incident proton energy for PTFE filters of differing thickness.
- b) Square filter macropixel design with thicknesses of PTFE in mm.
- c) Example of normalized scintillation of one macropixel after irradiation.
The proton-beam maximum energy along the target normal was measured by a time-of-flight detector [9], and on some shots, a dose-calibrated RCF stack was inserted into the beam to confirm the scintillator calibration. The SB-PBP filtering was the same as that shown in Fig. 1. The grid pattern caused by the differential-filter lattice is clearly visible in the inset in Fig. 2.

The raw CCD data from the PBP were split into macropixels as shown in Figs. 1. The CCD counts were then interpolated between the macropixels, as shown in Fig. 3a, on a nonlinear scale for a 5 μm stainless-steel target. Clearly, the CCD counts are larger for thinner filters. Also, the divergence of the signal narrows with increasing filter thickness. This narrowing of proton divergence with energy is typical for laser proton sources and is visible in the RCF data [5].

The proton-beam spectrum was then estimated using a least-squares fitting algorithm. From the RCF stack, the proton beam was found to typically exhibit a thermal spectrum well described by

$$\frac{dN(E)}{dE} \propto \frac{1}{E^{3/2}} \exp(-2E/E_0)^{1/2}, \quad (2)$$

where $E$ is the proton energy, $E_0$ is the beam temperature, and the spectrum extends up to a cut-off energy $E_m$ determined by the time-of-flight diagnostic. Using Eq. (2) and stopping curves like those shown in Fig. 1, the estimated photon output was calculated and compared with the experimentally measured photon output. Using the beam temperature $E_0$ and the total proton flux as fitting factors, the spectrum was then determined by the least-squares method. More details of the spectrum retrieval are given in Dover et al. [5].

This fitting procedure is carried out for each macropixel individually to give an estimated proton spectrum at each macropixel point. In Fig. 3b, the angularly resolved spectrum in the horizontal plane (along 4° in the vertical plane) is shown. As is typical from laser ion sources, the beam has a wide divergence that narrows with increasing energy. During the experiment, a systematic shift of the angle corresponding to the maximum proton energy was observed (in Fig. 3b, this is roughly 8° from the target normal, corresponding to a shift toward the laser axis). This has been determined to be due to nonthermal effects of the rear sheath expansion characteristic of ultra-short and ultra-intense laser pulses [10] and will be discussed in detail in a future publication.

We have therefore demonstrated the effectiveness of a scintillator-based beam-profile diagnostic to simultaneously measure the transverse beam profile and coarsely estimate the beam energy spectrum. We have carefully included the nonlinearity of plastic scintillators into our spectral retrieval to allow us to make accurate measurements of the absolute proton flux. We have shown that this diagnostic is effective in measuring protons in excess of 20 MeV. It would be difficult to increase this energy range because of an increasingly large background from energetic electrons that are also generated in the laser–plasma interaction. However, these can be eliminated using a time-gated CCD camera and fast-quenched CCD, which will be the subject of future research [5]. This novel diagnostic will therefore be of great interest to high-repetition-rate laser facilities and particularly for applications using laser-driven ion sources.

Acknowledgments

We thank the J-KAREN-P operations teams for their support, and M. A. Alkhimova, A. Ya. Faenov, Y. Fukuda, H. Kiriyama, A. Kon, K. Kondo, K. Nishitani, K. Ogura, T. A. Pikuz, A. S. Pirozhkov, A. Sagisaka, M. Kando, K. Kondo, T. Akagi, T. Yamashita, and the rest of the HIBMC team. We thank Nathan Cook for helpful discussions. This work was supported by a JSPS Postdoctoral Fellowship and KAKENHI Project No. 15F15772, and partially supported by JST PRESTO Grant Number JPMJPR16P9, Japan.

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Effect of target density in laser ion acceleration

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There has recently been much progress in compact laser systems, and laser ion acceleration is a compelling application of high-power compact lasers [1]. If a compact laser system could generate ions with sufficiently high energy, a low-cost compact accelerator would become feasible. However, the ion energies achieved to date are insufficient for some applications. Therefore, it is important to study which conditions are effective for generating ions with higher energies. Herein, we investigate a method to generate higher-energy ions and a high-quality ion beam with minimal energy spread.

Higher-energy protons can be obtained using a “light” material for the target. Herein, “light” denotes small $m/q$ (where $m$ is the ion mass and $q$ is its charge) and “heavy” denotes large $m/q$. A double-layer target is used because it can generate a high-quality proton beam (Fig. 1(a)) [2]. Carbon is employed as a “light” material for the first layer, and gold is used as a “heavy” material for comparison. Simulations are performed by varying the ion density (i.e., electron density) of the first layer with a fixed areal mass density. To examine the dependence of the achieved proton energy on the target density, we perform 3D and 2D PIC simulations. The number of ions (i.e., electrons) is the same in all cases, even under different densities. We increase the target density by reducing the thickness of the first layer while maintaining the same numbers of ions and electrons (Fig. 1(b)). We use a Gaussian linearly polarized laser pulse that is normally incident on the target. A laser power of 620 TW is focused on to a spot of size 3.2 μm (FWHM), with an intensity of $5 \times 10^{21}$ W/cm$^2$, a duration of 27 fs, and a laser energy of 18 J. The target is disk-shaped. The first layer has a diameter of 6.4 μm and its thickness is varied according to density, being 0.4 μm for $30n_c$, 0.15 μm for $80n_c$, etc., where $n_c$ indicates a critical density of $1.7 \times 10^{21}$ cm$^{-3}$. The ionization state of each ion in the first layer is assumed to be $Z = +6$. The hydrogen layer is narrower and thinner; its diameter is 3.2 μm and thickness is 0.024 μm.

Figure 2 shows the particle distribution and electric field magnitude of the $60n_c$ carbon case in a 3D simulation. After strong interactions with the target, part of the laser pulse is reflected, while another part is transmitted. The carbon ions are distributed over a much wider area by the Coulomb explosion.

The maximum proton energy is 110 MeV at $t = 267$ fs.

Figure 3 shows the obtained proton energy, which is normalized by its minimum in the carbon case, namely $E_{\text{min}}^{\text{C, min}}$, as a function of the initial electron density of the first layer, namely $n_{e,1}$. The obtained proton energy of the carbon case is much higher than that of the gold case. In the carbon case, the proton energy increases dramatically from $30n_c$ to $60n_c$ and is almost flat above $60n_c$. However, in the gold case, there is no such dramatic change in proton energy; instead, it decreases almost monotonically with density.

Figure 4 shows the electric field magnitude and the ion and electron distributions in the $60n_c$ carbon and gold cases at early simulation times. Also shown is the distribution of the electric field magnitude of the reflected laser on the $x$ axis. The head of the reflected laser has almost the same shape and value for both cases. The tail of the reflected laser in the carbon case is shorter than that in the gold case. In the $-22 \mu m < x < 0$ region, the electric field in the carbon case decreases much more rapidly than that.
in the gold case and quickly becomes almost zero. The reflected laser energy from the carbon ("light" material) target is much less than that from the gold ("heavy" material) target, even with the same initial densities of electrons and ions. This is one of the reasons why we can obtain high-energy protons from the carbon target; a "light" material target (LMT) experiences strong Coulomb explosions, resulting in it being much thicker than a "heavy" material target (HMT) in the early acceleration stage. This means that the electron density in the LMT becomes much lower than that in the HMT. Therefore, the reflection of the laser pulse decreases and the more laser energy is absorbed in an LMT. With an LMT, the reflected laser energy does not increase with target density above $60n_{cr}$. However, the gold target does not experience such a strong explosion. In an HMT, the reflected laser energy keeps increasing with density, meaning that the energy absorbed in the target decreases continuously. Therefore, the obtained proton energy decreases with target density.

The carbon target expands strongly in the $x$ direction, and this tendency becomes stronger with higher density. The stronger Coulomb explosion in the $x$ direction generates protons with higher energy. This effect increases along with density, ending only above a certain density, namely $n_0 > 60n_{cr}$ in our conditions. This is one of the reasons for the jump in proton energy and helps to explain the high-energy protons in high-density targets of "light" material.

The other reason for the jump in the obtained proton energy is the radiation pressure acceleration (RPA) behavior. The carbon ion cloud moves in the $+x$ direction. The velocities increase rapidly until around $60n_{cr}$, before becoming almost constant for $n_0 > 60n_{cr}$. This trend is also the same as shown in Fig. 3. However, the gold target does not experience such movement. The carbon-target velocities are much higher than the gold-target ones at all densities. This means that the RPA effect is much higher in the carbon target. In the initial stage of the RPA process, the electrons have almost the same momentum and distribution in the carbon and gold cases because they depend strongly on the laser conditions and the initial electron distribution. Therefore, the electric field working on the ions is almost the same in both cases. The "light" ions then acquire high velocities because they are "light". The RPA behavior is another reason why high-energy protons can be obtained from LMTs, which helps to explain the jump in proton energy in such targets.

The jump in proton energy of the LMT is due to the effect of the strong Coulomb explosion of the first layer and the effective RPA. The laser reflection from the LMT is smaller than that from the HMT. This also helps to explain why the obtained proton energies in the LMT are always higher than those in the HMT. HMTs have small target expansion and RPA effects with a large amount of laser reflection. Therefore, there is no energy jump as in LMTs and the obtained proton energy is low. Materials that can easily become "light" are ideal for the target because they can be almost fully stripped at low energy. It is effective for "lighter" ions to form quickly, before the main part of the laser pulse arrives, meaning an ordinary light material. That is, light materials are more effective than heavy ones for the target to obtain high-energy protons [3].

We have found that the obtained proton energy increases dramatically for a certain density of a light material target. That is, the Coulomb explosion of the target and the RPA act effectively above a certain density. Moreover, the reflection of the laser pulse from the target is small for a light material.

References
Laser-pumped plasma extreme ultra-violet (EUV) light sources have been investigated toward their application to next-generation microlithography.

It has been shown that an intense emission at the EUV wavelength ($\lambda = 13.5 \text{ nm}$) is obtained from Sn ions. In laser-produced plasma with electron temperatures of 20–50 eV, 4 to 14 times ionized Sn with the outermost electron subshell of 4d is produced, which has an intense photo-emission through 4d–4f and 4p–4d unresolved transition arrays (UTAs). The wavelengths of the emission are almost constant over these charge states and several emission lines overlap in the same wavelength region. In lower-density plasmas with an ion density less than $10^{19}/\text{cm}^3$, the contribution of the satellite lines from the inner shell or multiply excited states decreases, resulting in a narrow emission spectrum. Figure 1 shows the dependence of spectral efficiency on the temperature and ion density of Sn plasmas. The bandwidth (2%) of the EUV source is determined from that of the multilayer optics, and the fraction of usable EUV light for the lithography increases at lower densities.

A low plasma density is also preferable for reducing the effect of opacity, which also causes a broad emission spectrum. To produce low-density plasmas, CO$_2$ lasers are more suited for the pumping source because of the low critical density. To reduce the emission of particle debris, small droplets of Sn with a diameter of a few tens of micrometers are used as the targets of the EUV source. These mass-limited targets are expected to be also useful for producing low-density plasmas. However, the absorption of the CO$_2$ laser light by the droplets is inefficient because the target diameter is smaller than the beam size. Furthermore, the laser light is reflected from the steep density gradient of the plasma, which is produced at the droplet surfaces.

The double-pulse technique required to perform a plasma from the droplet targets is critical for obtaining a high-efficiency EUV source. As shown in Fig. 2, in recent studies, a YAG laser pulse with a duration of a few picoseconds irradiates the droplets to break the targets into particles through the effect of the shock wave. The cloud of particles expands up to 10 times the initial diameter ($=100 \mu\text{m}$) and is subsequently irradiated by the main CO$_2$ laser pulse with a duration of nanoseconds to produce a plasma with ideal density and temperature for EUV emission.

Radiation hydrodynamic simulations are a useful tool for optimizing the EUV source. However, conventional codes are not always applicable to low-temperature conditions when initially solid or liquid material is heated, evaporates to the gas phase, and is then ionized to produce plasma. The solid/liquid-to-gas transition may cause structure formation and particle emission. We have investigated this phenomenon theoretically and developed a hydrodynamic simulation code that takes account of the emission of particle debris from the heated metal targets.

We develop a Lagrangian hydrodynamic simulation code using grid re-organization algorithms, which allows one to place the grid along the distribution of particles and to evaluate the equation of state under the conservation of mass and internal energy.

The application of the Lagrangian hydrodynamics code to the modeling of laser-produced plasma has been limited by the collapse of grids because of the motion of the fluid. We use triangular grids in a two-dimensional geometry and the following grid re-organization algorithms to avoid collapse. As shown in Fig. 3(a,b), when the aspect ratio (i.e., the ratio of the cell height to the cell base) becomes too small or the cell becomes too flat, the cell is split, conserving its mass and internal energy. By contrast, if the ratio becomes too large or two grid points become too close, these points are merged and the cells are united.

![Fig. 1. Density and temperature dependence of spectral efficiency (solid line), which is defined by the fraction of in-band emission into 2% bandwidth at $\lambda = 13.5 \text{ nm}$ from total emission, and averaged charge (dotted line) of Sn plasma.](image1)

![Fig. 2. Schematic of the excitation of the LPP EUV source based on the double-pulse technique.](image2)
Formation of gas bubbles in the liquid phase, as well as formation of liquid clusters in the gas phase through phase transition, is modeled by splitting the target cell. The algorithms are shown schematically in Fig. 3(c,d).

We use the Van der Waals equation of state of Sn which determines the phase of the material for a given temperature and density, as shown in Fig. 4. The equation of state shows the two-phase region where the material is unstable as a uniform state and split into separate liquid and gas regions with a void ratio, which is determined as a function of temperature and density. In the present model, if the conditions of the target cell are found to be those for a two-phase region, the cell is split to produce separate liquid and gas cells. This forms a group of cells that conforms to a super-cell. Subsequently, the mass and internal energy of the target cell are redistributed to each cell to ensure the correct void ratio for the super-cell. Note that the temperature changes after the transition, which corresponds to the effect of latent heat, which arises from the difference in the internal energy between the liquid and gas phases. We use the method of time splitting, in which the hydrodynamic motion and re-organization of the grids are performed alternately for each time step.

We perform test calculations using the present code, whose results are shown in Fig. 5. We calculate the temporal evolution of the temperature and density of the cylindrical Sn target, heated uniformly at a fixed rate. Initially, the target is in the liquid phase, which evaporates into the gas phase. As shown in Fig. 5(a), for a moderate heating rate, the target expands through the two-phase region, showing that the initial small expansion causes the formation of bubbles inside the target, which grow in size and eventually break the target into particles. By contrast, for a large heating rate, because the temperature immediately exceeds the critical temperature (~7,000 K), the target expands uniformly without forming particles, as shown in Fig. 5(b).

The present model will be used to analyze the EUV source after further validations. Firstly, calculation of the particle formation due to the shock wave, which is driven by short, pre-pulse laser irradiation, will be carried out. Secondly, calculation will be extended to include the interaction between particles and the main laser pulse. Recently, the spatial distribution of density and temperature after the pre-pulse laser irradiation has been investigated. Comparisons with these experiments will improve our understanding of the mechanism of excitation of the Sn plasmas, which will be useful for further optimization of the EUV source.

References
Mo/Si multilayer-coated photodiode-based X-ray laser intensity monitor and its application to polarization analysis

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The laser-driven plasma soft X-ray laser (XRL) system at the Kansai Photon Science Institute, QST, provides 13.9 nm coherent radiation with a monochromaticity of 10⁻⁴ and a pulse duration of 7 ps, and has been used for various applications. To meet the increasing requirements for coherent pulsed beams, it is beneficial to determine the beam characteristics, especially the shot-to-shot beam intensity. The number of photons per pulse depends mainly on the excitation conditions of the pumping laser, and therefore, is quite sensitive to the gain of the lasing medium. A slight gain fluctuation leads to a large intensity variation, thereby indicating that a real-time beam-intensity monitor (BIM) is indispensable for quantitative XRL applications such as reflectivity and polarization measurements and pump-probe techniques.

Amplitude-division beam splitters such as free-standing and membrane-supported multilayer films have been used frequently as beam-intensity monitoring techniques at around 13.9 nm. The transmitted light for downstream experiments can be used without changing the direction of the optical axis, but there are several difficulties in fabrication process and operation of amplitude-division beam splitters, such as those resulting from membrane rigidity, roughness, uniformity, and absorption. Besides, reflector mirrors can be used as wavefront-division beam splitters, but the intensity distribution and pointing stability of an incoming beam strongly affect the susceptibility. Alternatively, photoionization-based gas detectors have a wide dynamic range and can be used effectively in the EUV range without changing the optical axis. However, they are unsuitable for use in the spectral regions in which the target rare gas has strong resonance. Furthermore, the installation and/or use would be restricted because of differential pumping.

The AXUV series of photodiodes (OptoDiode), commercially available silicon p-n junction photodiode detectors for EUV and X-ray radiation, are made of polished silicon, and some of them have an active area coated with a bandpass filter to filter out radiation outside a specific range, e.g., Si/Zr for the 11–18 nm range. Meanwhile, an AXUV photodiode coated with a well-designed Mo/Ba/C/Si multilayer has been reported to show a high reflectivity of 69.9% and work as a good polarizer at a wavelength of 13.5 nm and 45° incidence. Unfortunately, its use as a BIM has not been discussed explicitly. If a well-designed multilayer-coated photodiode shows high correlation between the reflected intensity and generated photodiode current at a wavelength of 13.9 nm, it should be possible to monitor the incident and reflected intensities from shot to shot. This type of BIM changes the direction of the optical axis but makes it possible to avoid the problems of amplitude- and wavefront-division beam splitters and can be installed easily anywhere in a beamline, even immediately in front of the samples.

To develop a reflection-type multilayer-coated photodiode for XRL, we prepared two identical AXUV100G photodiodes with an unfiltered active area of 10 × 10 mm². One of the photodiodes was coated with a Mo/Si multilayer by ion-beam sputtering; the parameters were determined to be a multilayer period of 10.36 nm and Mo thickness ratio of 0.34 by grazing-incidence X-ray reflectivity using Cu Kα radiation. The other photodiode was used without coating for detecting the reflected light from the MP in synchrotron radiation (SR) and XRL measurements.

The MP was characterized using SR from 12.5 to 15.2 nm. At 13.9 nm, the reflectance of the MP tilted at an angle of incidence of 45° was measured to be 52.5%, where R is defined as the ratio of the reflected beam intensity Io to the beam intensity when the MP is removed from the beam path. Note that both intensities have been measured with the OP irradiated at normal incidence. Meanwhile, the relative transmittance T has been measured to be 8.96%, where the definition is slightly different from conventional ones and is the ratio of the 45°-tilted MP signal, IOP, to a normal incident signal. Consequently, we obtain R/T = 5.86 and the sensitivity correction factor as α = 2.91, resulting from the difference between the respective independent photodiodes, in addition to the complete correlation between reflection and transmission intensities. It seems reasonable that the incoming beam to the photodiodes is absorbed almost completely and used to generate the photodiode currents proportional to the incident light intensity because the reflections from the MP and OP at normal incidence are negligible, being below 10⁻⁴. Therefore, IoP can be calibrated using R, T, α, and hIOP as

$$I_{O} = \frac{R}{T} \alpha \cdot h_{I_{O}}$$  \hspace{1cm} (1)

This indicates that the beam intensity can be monitored by measuring hIOP from shot to shot. Thus, MP performs well as a BIM that can deliver a high-intensity beam for application experiments.

Polarization analysis of XRL beams in single-target mode was performed using a six-axis soft X-ray ellipsometer installed at an end station of the XRL beamline. XRL beams were irradiated onto the MP active area and then reached the OP via a Mo/Si multilayer polarizing mirror (mirror A). The s- and p-polarization reflectances of A were determined with SR in advance, resulting in 54.5% and 2%, respectively, at an angle of incidence of 42.75°. Another plane mirror M2 of an unknown reflectivity R2 was placed between MP and A.

Figure 1(a) shows a plot of IoP versus hIOP for 23 successive shots, measured in the experimental configuration in which A is removed from the optical path, as illustrated in the inset. The correlation coefficient between IoP and hIOP is 0.965. Taking account of the reflectivity R2 of M2 placed between MP and OP, Eq. (1) is modified as

$$I_{O} = 17.1 \cdot R_{2} \cdot h_{I_{O}}$$  \hspace{1cm} (2)

Substituting the measured IoP and hIOP into Eq. (2), R2 can be evaluated from shot to shot, as shown in Fig. 1(b). The averaged reflectance is 0.568 ± 0.048, which is as high as that of A and a reasonable value because the multilayer coatings of A and M2 have been deposited in the same manner. Fig. 1(c) shows a SR and XRL; the XRL data agree well with the SR ones. The correlation coefficient between IoP and hIOP exceeds 0.960 comparison of the s-polarized reflectivities of A measured with
These results imply that the MP acts as a satisfactory BIM and enables absolute measurements with XRL. Figure 1(d) shows the reflectance of A plotted as a function of azimuth angle. By applying curve fitting to the sinusoidal data, we find that the XRL beam incident to A is perfectly linearly polarized with the polarization plane tilted slightly from the vertical direction, and that the polarization state at the end station is stable because of reflections by mirrors such as M2 on the beam path. Figure 1(e) shows the XRL beam-intensity stability, plotted using the IMP of 297 shots taken from the measurements in Fig. 1(c) and (d). Despite a large root-mean-square (rms) variation of 35%, quantitative polarization analysis can be performed successfully by means of the MP. The dark noise from the MP is negligible at below 0.2% rms with respect to the average MP signal. The large fluctuation is therefore considered to be caused mainly by the concentration fluctuation of the plasma at the source point and the shot-by-shot fluctuation of the pumping energy, in addition to the horizontal beam profile of the XRL output at the lasing medium. This indicates the importance of monitoring the beam intensity in real time during the experiments.

In conclusion, we have succeeded in developing an excellent XRL BIM by means of a Mo/Si multilayer-coated photodiode detector, enabling the delivery of a high-intensity beam to downstream experiments such as polarization analysis. We hope that our beam-intensity monitoring technique will be used widely in the time-resolved morphology of single- or multiple-shot laser ablation.

References

A new laser remote-sensing (LRS) system for inspecting social infrastructure constructions such as tunnels has been demonstrated. Laser hammering is an LRS procedure that can replace the hammer impact test for detecting defects inside concrete. The basic idea behind LRS is that a high-energy pulse of an impact laser system is irradiated on the concrete surface to generate panel vibrations by laser ablation and/or thermal stress, thereby acting as a hammer. After that, a laser interferometer detects the generated vibrations in the audible range, similar to the human ear. In recent years, we have demonstrated LRS (in the laboratory) using a laser system with a pulse energy of 1 J and a repetition rate of 25 Hz. The pulse energy of the impact laser should be increased to detect deeper and wider defects; this would also improve the signal-to-noise ratio in the LRS results because it would prevent noise being generated upon ablation. A higher repetition rate of the impact laser would also be an improvement because it would increase the LRS inspection speed. Figure 1 shows the distribution of the developed and commercial high-average-power laser systems currently in operation. For LRS, the output characteristics of the high-average-power laser system must exceed those demonstrated previously and fall within the shaded area in Fig. 1. Furthermore, the laser system should be able to operate under tough outdoor conditions and be suitable for commercial use. Therefore, it is important for the impact laser to combine environmental stability, compactable layout, and low cost.

The laser-irradiated medium should be cooled to prevent its thermal destruction when operating with high-average-power output; therefore, its temperature distribution is generated naturally using the cooling and pumping schemes. The thermal effects caused by the temperature distribution lead to distortion of the wavefront of the laser pulse, such as the thermal lens effect, and generate undesired effects in primary processes for which the laser phase is essential, e.g., focusing, propagation, and wavelength conversion. Most laser systems with an average power output of over 100 W are realized with special phase controllers such as a stimulated Brillouin scattering phase-conjugating mirror (SBS-PCM) or a cryogenic system, as shown in Fig. 1. Both advanced techniques are solutions for wavefront distortion by the thermal lens effect, but have some drawbacks for operation in outdoor conditions, in particular, large size and temperature control. In fact, an SBS-PCM requires a seed injection system to obtain a single longitudinal mode, while a cryogenic system requires various equipment and electrical power.

In this study, we developed an Nd:YAG laser system based on a master-oscillator power amplifier (MOPA) platform with a compact layout. LRS requires a simple and tough laser system with an adequate laser output. A commercial high-average-power Q-switched Nd:YAG laser (Liron Lasers, LPY742-100) was adapted as the master oscillator on an MOPA platform to downsize the amplifier stages. A single longitudinal mode was not required in the impact laser system because an SBS-PCM was not employed. Hence, a multi-longitudinal mode was adopted to achieve a low-cost master-oscillator system. Figure 2 shows the optical layout of the developed laser system. The wavelength and pulse width of the master oscillator were 1,064 nm and 14 ns, respectively. The pulses of the master oscillator were amplified with two 1.1 at% doped Nd:YAG rods pumped by flash lamps operating at 50 Hz. The Nd:YAG rods were 14 mm in diameter and 70 mm in length. The equal-sized Nd:YAG rods provided the same thermal effects and fluorescence spectra, allowing the components for thermal compensation to be simplified. However, the stored energy in the Nd:YAG rods could not be extracted sufficiently with a single pass of the master-oscillator pulse; therefore, a double-pass scheme was used for the first Nd:YAG rod amplifier. A design of the high power laser system considered for thermal-optical effect is important to prevent thermal lens effects in the amplifier rods. In the developed laser system, we installed pairs of lenses at the ends of the vacuum tubes to act as an image transfer tube (A to D in Fig. 2). The distance between each pair of lenses was adjusted with a translation stage to collimate the beam and correct the divergence that occurred because of the thermal lens effect. The size of the constructed laser system was 4.0 m × 0.8 m, including the master oscillator.

Figure 3 shows the input–output characteristics after single- and double-pass amplification by the first rod and amplification by the second rod for an input laser beam diameter of 13 mm. In Fig. 3, the symbols represent measured values and the solid lines are theoretical values estimated using the Frantz–Nodvik
formula, assuming a saturation fluence of 0.622 J/cm² for the Nd:YAG rod as a fitting parameter. The maximum value obtained for the output energy was 4.06 J with an operating frequency of 50 Hz. The measured output energies showed good agreement with the theoretical values, so the ASE could be neglected. Furthermore, thermal birefringence was cancelled appropriately in the double-pass amplification scheme. Saturation amplification was achieved after the double-pass scheme in the LRS laser system, but wavefront distortion led to undesired focusing characteristics. In the case of focusing with a simple lens with f = 687 mm, the beam profile at the beam waist showed an energy of 2.13 J was obtained. Moreover, the double-pass scheme in the first rod achieved full extraction of the stored energy during the amplification. The focusing characteristics are an essential parameter adequate laser irradiation on the concrete surface, and roughly 97% of the pulse energy was transferred successfully in an area twice that of the beam waist. The total electrical energy needed to run the system was roughly 20 kWh, which can be provided by a diesel generator or some storage batteries. A 20 kWh air-cooling system is also available. Therefore, the developed LRS system will provide standalone behavior without untransportable equipment in outdoor conditions.

Acknowledgments

This work was supported by the following programs: "Development of high-specification non-destructive inspection method for infrastructure constructions with laser technology" (representative: Dr. Katsumi Midorikawa in RIKEN) of the Council for Science, Technology, and Innovation, "Cross-ministerial Strategic Innovation Promotion Program (SIP)," and "Infrastructure Maintenance, Renovation, and Management" (funding agency: JST).

References

Deformation of a Molecular Orbital in Ethanol Induced by an Intense Laser Field

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In laser fields with intensities as high as $10^{14}$ W/cm$^2$, molecules are ionized through electron tunneling. It is understood that the tunnel ionization depends on the spatial density distribution and binding energy of the molecular orbital (MO) from which an electron is ejected. This is based on the angular dependence of the ionization probability measured for diatomic or triatomic molecules [1–5]. Recently, it has been suggested that MOs in molecules larger than the triatomic ones are deformed by laser electric fields [6,7]. As the molecular size increases, the energy spacing between MOs decreases, leading to strong interactions among MOs in laser electric fields.

In the present study, we derive the molecular frame photoelectron angular distribution (MFPAD) of the dissociative ionization of ethanol (CH$_3$CD$_2$OH) in an intense near-infrared laser field ($I_0 \approx 8 \times 10^{13}$ W/cm$^2$, $\lambda = 800$ nm). The energy levels from HOMO-1 to HOMO-4 are close in a small energy range of 3 eV. Additionally, photoelectron-photoion coincidence measurement with He(I) at 21.2 eV showed that electron ejection from different MOs results in different fragment ions [8]. Therefore, identifying the fragment ion allows us to identify the MO from which the electron was ejected.

In our experiment, we use a partially deuterated CH$_3$CD$_2$OH sample to avoid producing different fragment ions with the same mass. The vaporized sample is introduced into an ultrahigh-vacuum chamber through a micro-syringe [9], and the molecular effusive beam is irradiated with a circularly polarized laser pulse, which singly ionizes an unaligned molecule. A linearly polarized femtosecond laser pulse from Ti:Sapphire regenerative and multi-pass amplifiers ($\Delta \tau \approx 60$ fs, 1 kHz) is converted into a circularly polarized pulse by passing through a quarter-wave plate. The photoelectron drifts perpendicular to the laser electric field at the moment of ionization [3,4]. The recoil direction of a fragment ion reflects the orientation of the parent molecule. We detect an electron and a fragment ion in coincidence with two position-sensitive detectors to determine the angle between their recoil vectors. MFPADs are derived by taking account of the electron drift.

Figures 1A and B show the MFPADs of the CD$_2$OH$^+$ and CH$_3$CD$_2^+$ production channels, respectively. The CD$_2$OH$^+$ channel shows preferential electron ejection from the CH$_3$ side of CH$_3$CD$_2$OH (Fig. 1A), whereas the MFPAD of the CH$_3$CD$_2^+$ production channel is almost isotropic (Fig. 1B). A previous measurement using He(I) suggested that (i) CD$_2$OH$^+$ is produced from the first electronically excited state of the parent

Fig. 1. (A and B) Electron momentum distribution in the molecular frame for the CD$_2$OH$^+$ and the CH$_3$CD$_2^+$ channels, respectively. (C and D) Simulated MFPADs of HOMO-1 and HOMO-2 in a static electric field. (E) Simulated MFPAD of HOMO-1 without the influence of the electric field. The simulated results are convoluted with the experimental angular uncertainty ($\pm 45^\circ$).
CH₃CD₂OH⁺ ion and (ii) CH₃CD⁺ is produced from the second excited state of CH₃CD₂OH⁺ [8]. Therefore, the MFPADs of the CD₂OH⁺ and CH₃CD⁺ channels correspond to the electron ejection from HOMO-1 and HOMO-2, respectively.

We simulate the angular dependence of the tunnel ionization rate and compare it with the experimental results. We use density functional theory (DFT) with the KLR-SIC potential, which reproduces the HOMO binding energy. We solve the complex eigen-energy of the Kohn–Sham Hamiltonian under a static electric field and absorbing potential far outside the molecule. The tunnel ionization rate is obtained from the imaginary part of the Born–Garnow state eigenvalue [10]. Figures 1C and D show the simulated MFPADs for HOMO-1 and HOMO-2, respectively. The simulated HOMO-1 MFPAD (Fig. 1C) shows preferential electron tunneling in the direction along the CH₃ recoil and agrees reasonably with the measured one for the CD₂OH⁺ channel (Fig. 1A). Our simulations do not reproduce the measured HOMO-1 MFPAD unless we account for MO deformation in the electric field. Figure 1E shows the MFPAD for the field-free HOMO-1 from which the MO deformation is excluded. The MFPAD for the field-free HOMO-1 shows preferential tunneling in the lateral direction with respect to the CD₂OH⁺ recoil direction (Fig. 1E). This discrepancy suggests that HOMO-1 deformation is needed to explain the preferential electron ejection from the CH₃ side derived in the measured MFPAD of the CD₂OH⁺ channel.

For HOMO-2, the simulation indicates that the electron is ejected preferentially from the OH side (Fig. 1D). However, the measured MFPAD for the CH₃CD⁺ channel is almost isotropic (Fig. 1B). In the intense laser field, the second electronically excited state of CH₃CD₂OH⁺ can be produced by not only electron ejection from HOMO-2 but also from HOMO or HOMO-1 followed by the electronic excitation of CH₃CD₂OH⁺ to the second electronically excited state [9]. The isotropic MFPAD suggests that the stepwise channels contribute comparatively to the ionization to form the second excited state of CH₃CD₂OH⁺, which has a hole in HOMO-2.

In summary, we measure MFPADs of dissociative ionization channels of ethanol CH₃CD₂OH in a circularly polarized laser field with an intensity of I₀ = 8 × 10¹³ W/cm². The MFPAD of the CD₂OH⁺ channel shows reasonable agreement with the simulated MFPAD for HOMO-1. Our DFT simulations reveal that HOMO-1 is deformed appreciably by the laser electric field. The measured isotropic MFPAD of the CH₃CD⁺ channel cannot be reproduced by the simulated MFPAD for HOMO-2, suggesting that the electronic excitation following the electron ejection from HOMO and HOMO-1 takes place significantly.

Acknowledgments

The authors thank Ms. Yuko Hagihara for her support in the data analysis. The present work was supported financially in part by JSPS KAKENHI (Grant Numbers 22685004, 26288013, and 17K05089) and by the Consortium for Photon Science and Technology.

References

High-speed measurement of terahertz waveforms using a 100 kHz Yb-doped fiber laser for terahertz imaging

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Terahertz (THz) light has been used to inspect semiconductor devices, security, biological tissues, and other applications. THz light with low photon energy allows non-destructive and non-invasive probes to be used for these inspections without influencing the molecular structure and electronic properties. THz time-domain spectroscopy (THz-TDS) has been used widely as a sensitive and accurate method to observe THz spectra. This method has already been applied to two-dimensional THz imaging [1] and time-of-flight THz tomography [2] as an inspection tool.

To realize THz imaging as a practical tool, the acquisition speed of THz imaging systems must be increased by two to three orders of magnitude, as suggested in the 2017 THz science and technology roadmap [3]. In this study, we demonstrate the high-speed measurement of THz waveforms to improve the acquisition speed of THz imaging. First, we develop a laser system to generate intense THz pulses with a repetition rate of 100 kHz. Second, we construct a system for high-speed measurement of THz waveforms with the measurement time of 10 ms.

To achieve high-speed THz waveform measurement for practical use, we develop a compact system to generate intense and short THz pulses with high-repetition rate. Intense THz pulses allow us to measure samples with high absorbance into depth. The short THz pulses allow us to measure the thickness of thin films with high resolution.

To generate intense THz pulses, optical rectification in a LiNbO$_3$ (LN) crystal pumped by near-IR light with a tilted pulse front is commonly used [4]. Calculations suggest that near-IR pump light with a pulse width of around 350 fs (transform limited: TL) is best for effective THz light generation in this method [5]. Then, we develop a Yb-doped fiber laser system to generate pump light with a repetition rate of 100 kHz, a pulse width of 320 fs, and a pulse energy of 28 µJ, as shown in Fig. 1. To avoid enhancing the amplified spontaneous emission in the fibers, we divide the amplification process into six stages.

The output light from the Yb fiber amplifier is introduced into the small-tip device (16 × 20 mm$^2$) proposed in our previous paper [6]. In the conventional method, the pump pulse front is tilted by a diffraction grating and imaged onto an LN prism to obtain an intense THz output. Our device uses a “contact grating setup” in which the diffraction grating is placed in contact with the input surface of the LN substrate, thereby downsizing the THz light source drastically. Figure 2(a) shows the THz waveform obtained from the contact-grating device pumped by a parallel beam of 4 mm in diameter and 13 µJ. The peak electric field is around 1 kV/cm. The Fourier-transformed spectrum (Fig. 2(b)) shows a peak frequency of 0.6 THz and a bandwidth of 1.5 THz.

The slow acquisition speed in THz-TDS is due to scanning the optical delay line to obtain the temporal profile of the electric field, as shown Fig. 2(a). To overcome this problem, we place a retroreflector on a speaker diaphragm vibrating at 50 Hz to scan the optical delay quickly (Fig. 3). We can measure a single waveform with a scanning time range of 15 ps (Fig. 2(a)) by a measurement time of 10 ms, which is $10^4$ times shorter than the time required in the conventional method using the stepping scan. The 100 kHz laser system provides 1,000 data points during 10 ms, and therefore, the time interval between the data points is 15 fs. As described above, we realize a high-speed measurement system for THz waveforms with intense THz light. In the near future, we will realize high-speed THz imaging by using the system presented herein.
Acknowledgments

This work was supported partially by the Japan Science and Technology Agency (JST) under Collaborative Research Based on Industrial Demand “Terahertz-wave: Towards Innovative Development of Terahertz-wave Technologies”. We are grateful to Yuko Hagiwara for writing the image-capture software used in this work.

References


Fig. 2. (a) THz waveform and (b) Fourier-transformed spectrum obtained by our high-speed waveform measurement system. The inset shows our device used in this study.

Fig. 3. Schematic of THz-TDS system with fast-scanning delay line.
Method for Estimating Localization of DNA Lesions based on Fluorescence Anisotropy

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DNA damage induced by ionizing radiation can cause mutations and cancers. In particular, "clustered damage," namely a DNA region containing two or more lesions within a few helical turns, is rarely repaired. This damage is induced around high-linear energy transfer (LET) ionizing-radiation tracks, but the details of such damage are unknown. We have already developed a method for estimating the localization of apurinic/apyrimidinic (AP) sites or abasic sites (APs; see Fig. 1) on DNA using Förster resonance energy transfer (FRET) occurring between different fluorescent dyes (Alexa350 and Alexa488) (hetero-FRET) (Fig. 2). The FRET efficiency was calculated from Alexa350 fluorescence intensities before/after enzymatic digestion of the labeled DNA with APs [1]. We succeeded in estimating qualities of clustered APs produced in 4He2+, 12C5+, and 60Coγ-irradiated dry DNA films to study direct radiation effects using the method [2,3]. However, there are some problems associated with the complex protocol and the sensitivity due to the low extinction coefficient of Alexa350. Therefore, we developed "homo-FRET," which occurs between two or more Alexa488 molecules (Figs. 2 and 3). We can also obtain the FRET magnitude from the "fluorescence anisotropy" of homo-FRET between Alexa488 molecules. The new protocol using homo-FRET enables us to estimate DNA damage localization without any enzyme and improves the sensitivity to detect clustered damage. Herein, we present the results of the fluorescence anisotropy for DNA exposed to radiation and radio-mimetic chemicals.

PUC19 digested by Sma I was used (linear formed) for DNA samples to be irradiated. The DNA was dissolved in a 0.2M Tris-HCl (pH 7.5) buffer that was under cell-mimetic conditions in terms of radical scavenging capacity. 60Coγ-rays were used as a standard radiation source at the Kyoto University Research Reactor Institute. In addition, we used well-known high-mutagenic chemicals, namely methyl methanesulfonate (MMS) and neocarzinostatin (NCS).

We mixed the damaged DNA sample (10 μL in water) and 10 μL of 100 mM Tris-HCl (pH 7.5) in a microtube, added 2 μL of Alexa488/DMSO to the DNA solution, and incubated it for 24 h at 35°C. We purified the fluorophore-labeled DNA by ethanol precipitation followed by ultrafiltration, and then dissolved it in a buffered solution containing 80 wt% glycerin to prevent rotational Brownian motion of the fluorescent dye decreasing the anisotropy. We measured the fluorescence anisotropy at 525 nm (ex. 470 nm) using a spectrofluorometer equipped with a xenon arc-lamp (SPEX FluoroMAX-3, HORIBA-Jobin Yvon) at 10°C. The anisotropy <r> is defined as

\[ <r> = \frac{(I_{ex} - G \cdot I_{em})}{(I_{ex} + 2 \cdot G \cdot I_{em})} \]

where \( I_{ex} \) is the fluorescence intensity when the excitation and emission polarizers are both oriented vertically, \( I_{em} \) is that when...
the excitation/emission polarizers are oriented vertically/horizontally, and $G$ is the grating factor defined as $IHV/IHH$. The FRET efficiency can be calculated from $<r>$ by using a theory established by Runnels and Scarlata [4].

As shown in Fig. 3, the AP distribution for $^{60}$Co $\gamma$-rays is slightly more clustered than that for a random distribution. This suggests that $\gamma$-rays occasionally produce clustered APs compared to the case of a random distribution. $^{60}$Co $\gamma$-rays are categorized into low-LET radiation (~0.2 keV/µm). However, a low-energy secondary electron (LEE) around the track-end ejected by the photon has a few tens of electron volts per nanometer. Clustered APs can be produced by a single track of the LEE within a few helical turns of the DNA molecule.

MMS is a well-known alkylating agent. This methylates mainly on N3 and N7 of purine nucleobases. The methylated purines are easily released from DNA to produce APs. As can be seen, there seems to be two phases. At low AP density ($\lambda$), $<r>$ seems to be constant. However, for $\lambda$ higher than -1, $<r>$ decreases faster than the random distribution. The phenomena seen in MMS are due to differences in the alkylation rate of purines and in the release rate of the purine lesions.

NCS is an antibiotic holoenzyme that causes closely opposed carboxyl lesions under aerobic conditions because of its activated chromophore, diene-diyne diradical (Fig. 5). The $<r>$-$\lambda$ relation seems to deviate appreciably from the random distribution and from the other DNA-damaging agents tested here. The diradical leads to occasional production of closely bistranded lesions (clustered lesions) followed by DNA double-strand break (DSB). If the two closely opposed lesions labeled with the dye were produced by a single event, the anisotropy value at a low dose should be considerably less than $r_0$ (~0.343, $<r>$ without any FRET). However, the actual extrapolated value of $<r>$ at $\lambda = 0$ seems to be around $r_0$. This suggests that a single attack of NCS to DNA produces mainly single AP, but the resultant AP may attract another lesion within a few helical turns.

In conclusion, the present method will be useful for screening the mutagenicity and cytotoxicity of a chemical, an ionizing photon/particle with a given energy in terms of a new index, “AP clustering.” Because there are actually numerous types of DNA lesion as well as AP, particularly those induced by ionizing radiation, the method can discover only a part of damage clustering. However, reactive carbonyl lesions are generally produced not only directly but also indirectly by nature, e.g., by a base/nucleotide repair enzyme and by an amine. Therefore, using these additives to create carbonyls will widen the application range of the method.

We have tried to apply the method to a DNA sample irradiated with a heavy-ion beam to discover the complexity of clustered DNA lesions.

Acknowledgments

We thank Dr. Takeshi Saito of the Kyoto University Research Reactor Institute for helping with the $^{60}$Co $\gamma$-ray irradiation. We also thank Dr. Kengo Moribayashi and Mrs. Satomi Kayamura for helpful discussions and technical support. This work was supported by a Grant-in-Aid for Scientific Research (C: 16K00551) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

References


Fig. 4. Fluorescence anisotropy of AF488-labeled DNA exposed to $^{60}$Co $\gamma$-rays (● line a), MMS (▲ line b), and NCS (■ line c) as a function of averaged AP density. The bold line represents a random distribution [5].

Fig. 5. Active center of NSC chromophore. Although the diene-diyne moiety is structurally unstable, its apoprotein protects the chromophore from its chemical change. However, a sulphhydryl compound such as glutathione induces diradical production on the active center.
The animals and plants that thrive on Earth consist of many cells that are the bases of all life processes. To reveal the functions of cells in life processes, we must clarify the relation between cellular structure and function, for which high-resolution observations of the fine structures of intact biological cells in water with high resolution. In particular, soft X-ray microscopes studied as a new means of observing intact biological cells in water than visible light wavelength, X-ray microscopes have been observations of the fine structures of intact hydrated cells are cellular structure and function, for which high-resolution of cells in life processes, we must clarify the relation between cells that are the bases of all life processes. To reveal the functions to obtain an X-ray image of a 1-μm-thick cell at a resolution of 50 nm. However, X-ray illumination that intense damages the cell by breaking chemical bonds through ionization due to radiation and expanding the cell volume through heating due to X-ray absorption. Therefore, we seek to expose biological cells to short X-ray pulses of durations less than a few nanoseconds to obtain clear X-ray images without blurring.

Pulsed X-ray sources that uses a plasma produced by irradiating a target material with a high-intensity laser are called LPP light sources and are used as SXR light sources in laboratories. The SXR pulses emitted from the LPP are characterized by short durations (nearly equal to that of the excitation laser) and by emission wavelengths that depend on both the target material and specifications of the excitation laser. An LPP SXR source using a heavy-metal target (e.g., Au, W, or Bi) emits SXRs efficiently in the WW. Because a Au target is particularly suitable for WW SXRs, we use Au as the LPP target material. However, a large laser system that can produce laser pulses in excess of tens of joules is required to generate enough WW SXR photons to achieve spatial resolutions of less than 100 nm. This is the main reason why the contact-type SXRM is not yet available as an observation tool in the biological sciences, and a new intense pulsed SXR source is required.

In SXRM experiments using Gekko XII at the Institute of Laser Engineering at Osaka University, we found that the number of WW SXRs from a Au LPP increased in a gaseous N2 atmosphere [2]. The Gekko XII high-energy laser system has a wavelength, power, and duration of 1,053 nm, 120 J/pulse, and 500 ps, respectively. The target material was a thin Au film with 99.9% purity and 200 μm thickness. We used a flat-field spectrometer to measure the plasma emission spectra and a grazing-incidence spherical mirror to collect the SXR pulses and focus them on the entrance slit of the spectrometer. The X-ray pulses passing through the slit were monochromatized by a grating (4,800 grooves/mm) and recorded on an imaging plate (BAS-TR2025; Fujifilm Co., Japan), which was read using a laser scanner (Typhoon FLA 7000; GE Healthcare) with a 25 × 25 μm² pixel size. The spectral image was normalized over the entire area and read at 216 gradations as the emission intensity. The background of the emission intensity was obtained from an area of the spectral image without SXR exposure and subtracted from the emission intensity. The position of the emission distribution curve was translated to a wavelength on the basis of the grating equation, whereupon the wavelength was calibrated by the C and N edges.

The resolving power λ of the wavelength was estimated from the widths of the absorption edges and the value was less than 100. The 1,632-mm-long light path from the emission point to the imaging plate was filled with N2 gas. Figure 1 shows emission spectra from the Au plasma for N2 gas pressures of 0–400 Pa. Because of X-ray absorption due to the N2 gas, the emission intensity clearly decreases with pressure for wavelengths larger than the WW. Meanwhile, the emission intensities in the WW exceed those at zero pressure; the spectral intensity increases with pressure from zero up to 270 Pa and then decreases slightly at 400 Pa. The dip near 3.1 nm corresponds to the absorption peak of N2.

In this experiment, the emitted SXRs were absorbed by the N2 gas that filled the light path from the plasma to the detector. Therefore, we calculated the transmittance of the light path as a function of the gas pressure and then used the transmittance to calibrate the emission spectra. The results are shown in Fig. 2. The calibrated emission intensities clearly increase uniformly over a wide wavelength range.

The experimental results presented herein indicate that introducing N2 gas improved the conversion efficiency of the LPP SXR source. If N2 gas could be confined inside a small space around Au LPP (e.g., by using a gas cell or a pulsed gas jet), the absorption of the emitted SXRs would be decreased and a higher SXR intensity would be obtained at the sample point. The reported improvement in conversion efficiency makes possible single-shot SXR imaging of nanometer-scale samples in aqueous solutions using a compact pulsed laser system.

References
Fig. 1. Emission spectra from Au plasma for various N\textsubscript{2} gas pressures [2].

Fig. 2. Emission spectra from Au plasma normalized by N\textsubscript{2} transmittance [2].
Impact of Post-translational Modifications of Histone H3 K9 on Nucleosome Structure and Dynamics

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Post-translational modifications (PTMs) of histone proteins, such as methylation, acetylation, and phosphorylation, play important roles in epigenetics because they have been found to be targets of many proteins that change the chromatin structure and dynamics. The nucleosome is a fundamental structural unit of chromatin. The crystal structure was solved in 1997, revealing that the nucleosome is composed of around 150 base pairs of deoxyribonucleic acid (DNA) wrapped around a histone octamer consisting of two copies each of histones H3, H4, H2A, and H2B. The histone proteins have intrinsically disordered regions whose structures cannot be determined by X-ray crystallographic analysis or nuclear magnetic resonance (NMR) spectroscopy because they do not have stable conformations. Because the disordered regions are located in either the N-terminus or C-terminus of the histone proteins, they are known as histone tails. Such tails are biologically important because (i) they are known to stabilize the nucleosome structure and (ii) amino acid residues in the tails are subject to post-translation modification as epigenetic markers. However, the nature of the tails makes it difficult to characterize their conformations experimentally.

Chromatin undergoes extensive changes during the cell cycle and is required to be relaxed or condensed for the cell to execute vital biological programs such as gene transcription and DNA repair, replication, and recombination. Chromatin restructuring is facilitated by remodeling the motors that hydrolyze ATP and using the released energy to remove, exchange, or reposition nucleosomes, the primary subunits of chromatin. Many remodeling motors operate as large multiprotein complexes consisting of regulatory and accessory components organized around a catalytic subunit. Among the major human chromatin remodeling machines is the nucleosome remodeling and deacetylase (NuRD) complex. It contains the catalytic ATPase/helicase subunit CHD. The tandem PHD fingers of the CHD subunit have been shown to bind two histone H3 tails concurrently, thereby helping to direct or stabilize the complex at specific genomic loci. The bivalent engagement of the CHD PHD fingers is required for the repressive activity of NuRD and leads to the displacement of H1p17 from pericentric sites and dispersion of the pericentric heterochromatin mark of tri-methylation of Lysine 9th in histone H3 (H3K9me3). In addition, binding of the PHD fingers to histone H3 stimulates the ATPase activity and chromatin-remodeling function of CHD4 and can in turn be augmented by the ATPase domain.

To understand the molecular mechanics of the tandem PHD fingers, we carried out a comprehensive mechanistic analysis of the bivalent engagement of a pair of readers (the tandem PHD fingers of the CHD ATPase) with the intact nucleosome. We used various methods such as NMR, chemical reactivity assays, molecular dynamics simulation, and single molecule FRET experiments [1,2]. Here, we summarize the molecular dynamics results.

Using an enhanced sampling method named ALSD that we developed recently [3,4], we studied the impact of acetylation and methylation on the 9th residue Lys of H3 tail in a nucleosome context. This method is essential because the tails are intrinsically disordered regions and do not adopt stable conformations. Therefore, intensive conformational sampling must be performed to characterize the conformation. In doing so, we carried out 256 independent simulations with different initial conformations. The initial conformations were prepared using a 2-ns-long MD simulation under a condition where interaction energies were intentionally reduced to enhance conformational changes, starting from an extended form of histone H3 tail with different initial velocities. We performed the ALSD production run for 7.68 μs (= 30 ns × 256 runs) in total after ALSD iterative runs to realize a random walk on the λ axis. The conformational ensembles obtained by a production run of the same simulation length were analyzed after reweighting at λ = 1 based on a reweighting scheme, which corresponds to conformations under physiologically relevant conditions (300 K and 1 atm). The weight for each conformation in the ensemble indicates a relative existence probability.

The results show that irrespective of the presence or absence of the PTMs, the H3 tail remains in contact with the DNA [3]. The spatial distribution of the histone H3 tail in the conformational ensemble showed that the entire tail in NCP almost always interacts with nucleosomal DNA (Fig. 1). The H3 region encompassing residues 1–9, which are targeted by the PHD fingers, occupies both major and minor grooves of the outer DNA and forms transient hydrogen bonds with the phosphate groups of DNA. When K9 is tri-methylated or acetylated, the distributions of the tails change drastically. Essentially, irrespective of the PTMs, the tails are located along the DNA. However, upon the PTMs, the spatial distributions are limited compared to unmodified K9. Furthermore, the solvent-accessible surface area (SASA) of residues 1–9 of H3 increases for K9me3 (Fig. 2). This can be interpreted as follows. Exposing the hydrophobic methyl moieties to the solvent destabilizes the molecule. This is compensated by further exposing the hydrophilic residues in the tail. These conformational changes due to the PTM may provide a stable scaffold for the PHD fingers.

In this study, together with NMR, chemical reactivity, and FRET experiments, we show that binding of the paired PHDs to NCP is decreased compared to their binding to the free H3 peptide. NMR, chemical reactivity, molecular dynamics, and FRET analyses point to a critical role for intra-nucleosomal histone-DNA interactions, which reduce the accessibility of H3 tails in NCP and impede binding of the readers. We demonstrate that the histone-binding activities of paired PHDs toward NCP differ, with PHD2 initiating the interaction that is further modulated by the linker between the domains and by nucleosomal DNA. Our findings reveal a distinctive regulatory mechanism for the association of paired readers with the nucleosome, which provides an intricate balance between cooperative and individual activities of the readers.
Fig. 1. Spatial distributions of K9 tip obtained by molecular dynamics simulations: (a) unmodified K9; (b) K9ac; (c) K9ac.

Fig. 2. Differences in solvent-accessible surface area (SASA) for each amino acid in H3 tail. Orange and brown lines denote the difference between K9ac and unmodified K9 and that between K9me3 and unmodified K9, respectively.

Acknowledgments
The author is sincerely grateful to all lab members for their critical comments and suggestions regarding this work. This research was funded by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Strategic Programs for Innovative Research, Computational Life Science and Application in Drug Discovery and Medical Development (hp140029, hp150233, hp160223, hp170255) and by JSPS KAKENHI (No. 25116003).

References
DNA conformational transitions inferred from re-evaluation of difference electron density maps

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DNA plasticity is important in various biological processes such as transcriptions and packaging of genomic information. A representative example of such plasticity is the sequence-dependent deformation of DNA, which is known to be crucial for molecular recognition of DNA-binding proteins. The deformation is strongly related to the conformational transitions of the phosphate backbones of DNA.

Of the few studies that have used crystallography to analyze DNA flexibility, most used the crystallographic B-factor [1, 2]. Related to atomic thermal motion, the B-factor is expressed as the probability density function of atomic displacement from the mean position. However, it is difficult to use the B-factor to capture large conformational changes such as phosphate backbone transitions because the distribution of atomic positions in the crystal is assumed to be only spherical or elliptical in the B-factor calculation.

To deal with the variety of molecular conformations in crystals, assignments of multiple conformations have been performed. In some cases, multiple conformations of phosphate backbones were identified. However, those identifications were usually limited to high-resolution crystal structures. Recently, investigation of 2Fo–Fc electron density maps of protein structures have been reported to reveal unidentified minor conformations of protein-side chains, even in modest-resolution crystal structures [3]. In the present study, to evaluate the possibility of conformational transitions of DNA, electron density maps of DNA crystal structures were analyzed comprehensively [4].

In this study, we used the difference electron density map (mFo–DFc) to discover unassigned conformational transitions. Such a map represents the differences between structure factors derived from experimental X-ray diffractions and those calculated by Fourier transform of the model coordinates. Therefore, we expect such maps to provide us with information about structural transitions that were neglected in the refined models.

From the Protein Data Bank, public database of biomolecular structures, we extracted 147 sets of coordinates and X-ray structure factors of DNA solved at a resolution equal to or better than 1.5 Å. After refining the individual B-factors, we then recalculated the difference maps and extracted peaks from them. We set the threshold of the peak intensity to 3.5σ.

We began by examining the distribution of distances between peaks and their nearest DNA atoms. As shown in Fig. 1, peaks were often observed at around 1.25 Å and 3.0 Å from the DNA. Most peaks around 3.0 Å from the DNA are considered to correspond to unassigned solvent atoms, because low-occupancy solvent atoms are not be assigned in the refinement procedure in general. The peaks found around 1.25 Å are inferred to arise from the movement of the DNA itself: the distances from the DNA are too short to be interpreted due to the densities of the other molecules and too long to be interpreted due to the thermal vibration of the atoms around their mean positions. Therefore, we concluded that the peaks correspond to conformational transitions rather than to thermal vibrations of individual atoms.

Next, we calculated the peak frequency of each atom of DNA (Fig. 2). The frequencies are around 5% for base atoms. By contrast, the peak frequencies for the atoms in sugar and phosphate are higher, namely 8–27%. In particular, P atoms most often accompany difference densities. As shown by using NMR and MD, phosphate backbones are equilibrated with different conformations in solution. Therefore, the peaks here most likely correspond to different backbone conformations in crystal.

We then classified the dinucleotides of our dataset according to known DNA conformation clusters and examined the differences in the distributions of the P-atom peaks due to the conformations. These distributions differed considerably among the conformations. The peaks were highly localized in the A/B, ZI, and ZII conformations (Fig. 3). This indicates that the movement of phosphate is strongly restricted to one direction for these three conformations. The locations of the

![Fig. 1. Distances between peaks in the difference electron density (mFo–DFc) maps and their nearest DNA atoms.](image1)

![Fig. 2. Peak frequency of each DNA atom in the difference map. To calculate the peak frequency, peaks at distances within 2.2 Å from the DNA atoms were considered.](image2)
peaks found in ZI were consistent with those of P atoms of known alternative ZII conformation (Fig. 3, left). The peaks in ZII were found in locations corresponding to those of P atoms in the ZI conformation. Therefore, the peaks for ZI and ZII correspond to transited P atoms. Similarly, we interpret most of the peaks for A/B as transitions from A/B to BI.

Finally, we discuss the local environment of the DNA molecules on the ZI/ZII transitions. Many Z-DNA crystal structures for d(CGCGCG) have been solved in the same crystal system, namely P2_12_1_21 with a = 17.8 Å, b = 31.2 Å and c = 44.3 Å (Table 1). Guanine N7 at the sixth residue in chain A is a metal cation coordination site in the crystal structure. Upon closer observation, we found that the cations are intimately associated with the polymorphisms of phosphate of the fifth residue in the same chain. When guanine N7 at the sixth residue is coordinated directly by cations, ZI/ZII polymorphism at the fifth residue tends to be suppressed, and hence, ZII conformation is preferable, as summarized in Table 1. Electron density maps for the representative structures of the fifth phosphates are shown in Fig. 4. When guanine N7 at the sixth residue is coordinated by cations, five water molecules are coordinated octahedrally to the metal ion, as shown in 4HIG. One of the water molecules stabilizes the ZII conformation of the fifth phosphate by interacting with atom OP1 of the phosphate. This hydrogen-bond network disappears when there is no cation at this site (e.g., 1DN5). Interactions between polyamines and the fifth phosphates are sometimes observed in addition to metal binding (Table 1). These interactions cooperatively stabilize the ZII conformations of the phosphates. Interestingly, the authors of 3WBO structure themselves assigned ZI/ZII transitions, which indicates that the transition in this structure is more obvious than in other structures. This specimen was thoroughly demineralized using liquid chromatography and no divalent cations were included in the crystallization condition. Removing divalent cations probably induces ZI/ZII transitions. Therefore, the hydrogen-bond network initiated from the divalent cations is important for determining the state of the phosphate backbone transitions.

Our analysis indicates that the electron density maps contain much structural information and that phosphate backbones assume rather polymorphic conformations even in crystals. Such information deepens our understanding of the nature of DNA conformations.

### Table 1. ZI/ZII transitions in Z-DNA crystal structures

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### References
Fractal nature of relaxor ferroelectrics

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Relaxor ferroelectrics exhibit many unique and useful properties, such as large dielectric and piezoelectric coefficients with broad temperature and frequency dependencies. They have attracted intense scientific and industrial interest over the past few decades because they often show complex multiscale structures and puzzling mechanisms. Because of their good piezoelectric properties, relaxor ferroelectrics also show strong potential for industrial applications such as transducers. However, despite intensive research, the intrinsic mechanism underlying the unique properties of lead-based relaxors remains unclear. A main reason for this is the necessity to deal with the nanometer-to-micrometer-scale heterogeneity that is intrinsic to relaxors.

Typical relaxors have PbB'B''O₃ complex perovskite structures, where two different ions occupy the perovskite B site stoichiometrically to conserve the average charge of 4+, for example, Pb(Mg₁/₃Nb₂/₃)O₃ (PMN) and Pb(In₁/₂Nb₁/₂)O₃ (PIN). However, the arrangement depends strongly on the actual materials. The randomness at the B site is commonly accepted to be intrinsic to the appearance of the relaxor state.

PIN [1,2] is one of the best materials for investigating how the randomness at the B site affects the relaxor nature. Annealing PIN crystals orders the In and Nb atoms along the 111 direction, whereas quenching leads to disorder. PIN with a large amount of In-Nb ordered region (ordered-PIN: O-PIN) transforms into an antiferroelectric (AFE) state, while that with a large amount of In-Nb disordered region (disordered-PIN: D-PIN) becomes a relaxor. The dielectric constant $\varepsilon'(T)$ exhibits a small but sharp drop at a transition temperature $T_N$ around 430 K in O-PIN, and by contrast, a large and broad peak around $T_{max}$ near room temperature (RT) in D-PIN, where $T_{max}$ depends strongly on the frequency of the electric field.

The structure and dynamics of relaxors can be understood in terms of fractals, which can deal well with a broad distribution of length and time scales [3,4]. However, few reports exist that treat the structure and dynamics in a unified approach. The present study addresses the issue using transmission electron microscope (TEM), synchrotron diffuse X-ray scattering (SDXS), and quasi-elastic light scattering (QELS) experiments on PIN to investigate the distribution of spatial structures and dynamics by changing the randomness at the B site.

Figure 1 shows the nanostructure in D-PIN observed by the TEM technique [5]. The white and black regions correspond to polar and non-polar regions, respectively. The pattern is characteristic because it remains similar if we magnify any given region, thereby showing that the sample has self-similarity (i.e., a fractal nature).

To confirm the fractal nature quantitatively, we performed SDXS measurements. Figure 2(a) shows the temperature evolution of the scattering intensity as a function of momentum transfer corresponding to the spatial size of interest [5]. Power-law behavior is clear in the log-log plot, indicating that a self-similar structure appears at low temperatures. The change in slope corresponds to the change in the fractal dimension ($D_f$). $D_f$ reaches 2.5 at 100 K, indicating that the relaxor D-PIN is near the percolation threshold at that temperature. We used the QELS technique to measure the dynamics from the self-similar structure, and confirmed that these dynamics also showed power-law behavior (Fig. 2(b)) [5].

In conclusion, we have confirmed unambiguously the fractal nature of the relaxor D-PIN for the first time by the complementary use of the TEM, SDXS, and QELS techniques. No such fractal nature was observed in the antiferroelectric O-PIN, in which the randomness at the B site is excluded [5]. We expect that such fractal nature is common to inhomogeneous but functional materials that show large susceptibility, and introducing randomness is key to realizing such properties.

References
Fig. 2. Results of (a) synchrotron X-ray diffuse and (b) light scattering measurements of D-PIN. The plots are displayed on logarithmic scales. The regions indicated by the solid lines show the existence of a self-similar structure in the system, and the slopes correspond to the fractal dimension of the system.
Hydrogen forms various chemical bonds in materials.\(^1\) Because of this bonding flexibility, hydrides exhibit various functionalities such as hydrogen storage, superconductivity, and fast ionic conductivity. Hydrogen-rich materials are expected to show excellent functionalities.

Complex transition-metal hydrides are a class of materials with high hydrogen content, in which hydrogen atoms are covalently bonded with transition-metal atoms to form complex anions. For example, iron-containing complex hydrides consist of octahedral \([\text{FeH}_6]^{4-}\) complex anions and metal cations. This six-fold hydrogen coordination realizes high hydrogen contents of iron-containing complex hydrides.\(^2\) In the present study, we tried to synthesize a rare nine-fold hydrogen-coordinated complex hydride.\(^3\)

The thermodynamical stability of a novel complex hydride \(\text{Li}_5\text{MoH}_{11}\) was evaluated by first-principles calculations. The theoretical calculations predicted that \(\text{Li}_5\text{MoH}_{11}\) can be synthesized via the reaction \(5\text{LiH} + \text{Mo} + 3\text{H}_2 \rightarrow \text{Li}_5\text{MoH}_{11}\). \(\text{Li}_5\text{MoH}_{11}\) was predicted to consist of \([\text{MoH}_9]^{3-}\) nine-fold hydrogen-coordinated complex anion, five \(\text{Li}^+\) ions, and two \(\text{H}^-\) ions. We tried to synthesize the theoretically predicted \(\text{Li}_5\text{MoH}_{11}\) using a high-pressure technique and to clarify the existence of the theoretically predicted nine-fold hydrogen coordination.

We developed a high-pressure technique to hydrogenate metals under high pressure and high temperature.\(^4\) This technique enables us to hydrogenate a sample approximately 1 mg in weight, which is suitable for in situ X-ray diffraction measurements. In the present study, it is necessary to determine the hydrogen position, making neutron diffraction measurement indispensable (a deuteride is used for neutron diffraction measurement instead of the corresponding hydride). The neutron diffraction measurement requires a large sample of more than 10 mg. We developed a high-pressure technique to synthesize a large sample of several tens of milligrams for a neutron diffraction experiment. The development was carried out with the aid of in situ synchrotron-radiation X-ray diffraction measurement (Fig. 1). A powder mixture of \(\text{Mo}\) and \(\text{LiD}\) with a molar ratio of 1:6 was prepared by mechanical milling at 400 rpm for 4 h under an Ar atmosphere. The mixture was compacted into a disk 4.0 mm in diameter and height. The disk was placed in a capsule made of pyrolytic boron nitride and sealed in a hydrogen sealing capsule made of NaCl together with an internal deuterium source (\(\text{AlD}_3\)). The sample was pressurized to 5 GPa at room temperature and deuterized at 923 K for 24 h. The deuterized sample was cooled to room temperature and then depressurized to ambient pressure.

The recovered sample was yellow in color, indicating that the deuterized sample was a complex transition-metal deuteride. The recovered sample was then subjected to neutron diffraction measurements. The obtained diffraction data were analyzed by the Rietveld method. Figure 2 shows the crystal structure of \(\text{Li}_5\text{MoD}_{11}\) determined by the Rietveld analysis. The obtained crystal structure agreed well with the theoretically predicted one; the novel complex hydride \(\text{Li}_5\text{MoD}_{11}\) was synthesized with nine-fold hydrogen coordination.

Such hydrogen-rich materials are expected to exhibit high-critical-temperature superconductivity if the gaps close under high pressure. Another preliminary calculation shows that at least one stable metallic phase of \(\text{Li}_5\text{MoH}_{11}\) is stable above 94 GPa.\(^3\) Fast lithium conduction is also expected because of significant rotational motion of the \([\text{MoH}_9]^{3-}\) complex anions.

There has been active research on the superconductivity of strongly correlated electron systems since the discovery of high-\(T_c\) cuprates. The superconductivity mechanism of a strongly correlated electron system is considered to differ from that of conventional superconductors. Understanding this mechanism is expected to lead to design guidelines for new high-\(T_c\) superconductors. It is well known that the superconductivity of strongly correlated electron systems exhibits a superconducting dome in the vicinity of the magnetic order. There is considered to be a close relation between superconductivity and magnetic fluctuations. Recently discovered iron-based superconductors have attracted interest in their superconducting mechanism. As a typical iron-based superconductor, iron pnictide shows a superconducting phase near the antiferromagnetic phase, which is accompanied by a tetragonal-to-orthorhombic structural transition with significant electronic anisotropy (nematicity). This indicates that the fluctuations in electronic nematicity are closely related to the superconductivity in addition to the magnetic fluctuations. However, because both fluctuations appear under very similar conditions, they are difficult to distinguish.
To address this issue, we focus on changes in the physical properties of the iron-based superconductor due to chemical and physical pressure effects. FeSe shows electronic nematicity below $T_s = 90$ K without magnetic ordering at ambient pressure. This nematicity is suppressed by substitution of Se with S (applying chemical pressure) without inducing magnetic order. By contrast, the electronic nematicity is suppressed by physical pressure. However, magnetic ordering is also induced, and $T_c$ is enhanced up to 40 K around 6 GPa. Therefore, systematic study of temperature-pressure-substitution effect of FeSe$_{1-x}$S$_x$ can provide information about electronic nematicity, magnetic ordering, and superconductivity independently.

As a result of high-pressure resistivity measurement, we observed separation of the partially overlapping nematic and magnetic phases by increasing the amount of S substitution. In addition, a new superconducting state was observed in this region. With further increase in S concentration, the nematicity disappeared completely and the magnetic ordering shrunk. As this magnetic phase changes, the superconducting region in the $P$-$T$ phase diagram becomes dome-like.

To verify the separation of nematicity and magnetic ordering, we approached from the viewpoint of the crystal structure. The synchrotron-radiation X-ray diffraction measurement was carried out using the diffractometer for diamond anvil cells installed at beamline BL22XU in SPring-8. A single-crystal specimen was loaded into a diamond anvil cell with a helium pressure medium, which guaranteed hydrostatic conditions even at high pressure and low temperature. The diamond anvil cell was mounted in a closed-cycle helium refrigerator with a gas membrane for maintaining constant pressure upon cooling. The pressure in the sample space was determined by ruby fluorescence methods for the whole temperature range.

From high-pressure X-ray diffraction measurements of FeSe$_{0.92}$S$_{0.08}$, no structural changes were observed in the region between the nematic and magnetic phases, while the magnetic phase shows lattice distortion (Fig. 3(b,c)). In this region, $T_c$ is enhanced. This result suggests the formation of a new superconducting state in FeSe$_{1-x}$S$_x$. We also found differing influences of the chemical and physical pressures on the crystal structure, in particular, the chalcogen height $h_{Ca}$ from the iron plane.

This study has revealed that the high-temperature superconductivity in FeS is closely related to the magnetic ordering and not to the electronic nematic state. The above research results provide important information for understanding the mechanism of the high-temperature superconductivity of iron-based superconductors.
Observation of Magnetic Circularly Polarized Emission in the X-ray Region

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A new magneto-optical effect is reported in the hard X-ray region. The new effect is an X-ray analog of magnetic circularly polarized emission (MCPE) in the visible region, which is a phenomenon whereby photons emitted from a magnetized material are circularly polarized. The degree of circular polarization is measured for the $K\alpha$ emission of metallic iron and is found to be large (~12%). It is also found that the sense of the circular polarization is reversed when the magnetization of the sample is reversed. These results constitute evidence that MCPE exists in the hard X-ray region. The observed large dichroic effect is also a feature suggesting that the new effect can be applied to a new measurement technique for practical materials.

The circular polarization of light is related to the magnetization of materials through symmetry and this fact gives rise to a magneto-optical effect. An obvious example is magnetic circular dichroism (MCD), which is the difference between absorption cross-sections when the circular polarization of incident light is parallel and antiparallel to the magnetization of a sample. Although the Faraday and magneto-optical Kerr effects are phenomena whereby the polarization plane of linearly polarized light rotates after transmission through and reflection from a magnetized sample, respectively, they are consequences of a difference between refractive indices of right and left circularly polarized light in a magnetized medium. Magneto-optical effects are very basic phenomena involving light and magnetism and now play vital roles in applications such as optical isolators and magneto-optical Kerr microscopes.

Because X-rays are a form of light, magneto-optical effects also exist in the soft and hard X-ray regions. The advent of synchrotron X-ray facilities has provided intense, highly tunable, and energy-tunable X-rays and has enabled us to observe magneto-optical effects in the X-ray region. Following the discovery at DESY of MCD in the hard X-ray region [1], major X-ray magneto-optical effects were reported in 1990s [2–4]. In particular, X-ray MCD is now a standard technique in research on magnetism because of several advantages, namely (i) element selectivity due to core-level spectroscopy; (ii) applicability of magneto-optical sum rules at spin-orbit split edges; and (iii) modestly good lateral resolution due to well-collimated synchrotron X-rays.

However, a problem with X-ray MCD is the very small dichroic effect (~0.5%) in the hard X-ray region for 3d transition metal (TM) elements. The use of hard X-rays is indispensable for bulk-sensitive measurements because of the long penetration length of hard X-rays into the materials. In addition, 3d TM, which include Mn, Fe, Co, and Ni, are crucial elements in magnetic materials. Accordingly, there has been strong demand for finding a new principle or technique that would allow element-selective X-ray measurements with a large dichroic effect for 3d TM elements in the hard X-ray region.

Magnetic circularly polarized emission (MCPE) is a magneto-optical effect and a phenomenon whereby photons emitted from a magnetized material are circularly polarized. In 1971, Marrone and Kabler reported that the luminescence of excitons in alkali halides is markedly circularly polarized under magnetic fields [5]. Surprisingly, MCPE is yet to be reported in the X-ray region. For instance, the $K\alpha$ emissions of 3d TMs are well-known characteristic X-rays in the hard X-ray region and correspond to transitions from the 2p level to the 1s level. The final state of $K\alpha$ emission is the 2p$^2$ state and has large spin-orbit coupling, which is an essential requisite for a magneto-optical effect. A considerable interaction between the 3d magnetic moments and the 2p hole spin is also known [6]. A large dichroic effect is thus expected in $K\alpha$ emission. To address the aforementioned challenging issue, a measurement of circular polarization in $K\alpha$ emission is therefore planned here for metallic iron [7].

Experiments were carried out at beamline BL22XU at SPring-8. The experimental setup is described below and illustrated in Fig. 1. The sample was an iron single crystal that was inserted between permanent magnets to saturate the magnetization. The sample was illuminated by intense incident X-rays generated from an undulator. Fluorescence X-rays emitted from the sample were collimated by an exit slit (slit 1) down to 120 µrad in divergence. This is most important because the optical elements mentioned below are based on crystal optics. The quarter-wave plate (QWP) was a diamond single crystal that mutually converts circularly and linearly polarized X-rays. The polarization analyzer that reflects the vertical component of the incoming fluorescence X-rays was a Ge single crystal, which also functioned as an energy analyzer. The combination of a QWP and a polarization analyzer is a standard device for detecting the circular polarization of a beam of photons. Ideally, the intensity at the detector equals $I_0(1-P_c)/2$ ($I_0(1-P_c)/2$) when the QWP generates a π/2 (~π/2) phase shift, where $I_0$ is the total intensity and $P_c$ is the degree of circular polarization.

Fig. 1. Top view of experimental layout. QWP: a diamond phase retarder that acts as a quarter-wave plate. Analyzer: a Ge(400) single crystal that is both an energy and a polarization analyzer.
The obtained Fe $K\alpha_1$ emission spectra are shown in Fig. 2(a). $I^+$ (red open circles) and $I^-$ (blue closed circles) are data observed when the $\pi/2$ and $-\pi/2$ phase shifts, respectively, are introduced by the QWP. The magnetic field is applied as shown in the inset and is defined as positive. It is obvious that the $I^+$ spectrum is shifted to the low-energy side compared to the $I^-$ spectrum. This difference between the two spectra is direct evidence that the $K\alpha_1$ emission is circularly polarized. The difference spectrum $I^+ - I^-$ normalized by the peak intensity of the sum spectrum is shown in Fig. 2(b) as magenta solid circles. When the magnetic field (and therefore the magnetization of the sample) is reversed, the sense of the circular polarization is reversed, as shown by the green open circles, which are data measured when the magnetic field is directed along the positive and negative directions, respectively. Solid lines are a guide to the eye.

These results clearly illustrate that (i) the energy-resolved $K\alpha_1$ spectrum of ferromagnetic Fe indicates finite circular polarization and (ii) the circular polarization is inverted when the magnetization of the sample is inverted. These two features unambiguously indicate the existence of MCPE in Fe $K\alpha_1$ emission. The flipping ratio $(I^+ - I^-)/(I^+ + I^-)$ is a measure of the size of the dichroic effect and was $12 \pm 4\%$ at 6.405 keV. If the scattering-angle correction and QWP efficiency are considered, the value would amount to $18 \pm 6\%$. Because the flipping ratio of metallic iron in soft X-ray MCD is around 30\%, a dichroic effect comparable to that in the soft X-ray region is obtained in the hard X-ray region.

To summarize, it is confirmed experimentally that MCPE exists in X-ray core-level emission and that the dichroic effect is quite large even in the $K$-edge of 3$d$ TMs. Hence, this magneto-optical effect may open a new way to perform element-selective and truly bulk-sensitive measurements of the magnetization of 3$d$ TMs.

References
Adaptive design of an X-ray magnetic circular dichroism spectroscopy experiment with machine learning

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Materials informatics, namely materials science reinforced with information science, has blossomed with the recent developments of machine-learning (ML) techniques such as convolutional neural networks. Materials informatics is aimed at the efficient discovery and development of novel materials with the assistance of ML. At the same time, metro-informatics, namely measurement techniques involving information science, is necessary for accelerating materials informatics.

Spectroscopy is one of the most important uses of quantum beams such as synchrotron X-rays. X-ray spectroscopy reveals the electronic structures of materials by exciting the core or valence electrons. X-ray magnetic circular dichroism (XMCD) spectroscopy, a variation of X-ray absorption spectroscopy (XAS), is particularly important for investigating magnetic materials such as permanent magnet materials, magnetic recording, and spintronic materials. Spins and orbital magnetic moments of a specific element can be evaluated by XMCD spectroscopy using magneto-optical sum rules. In this study, we applied an ML technique to an XMCD spectroscopy experiment to improve its efficiency.

Known as kriging, Gaussian process (GP) regression is an ML technique that is used in geostatistics to predict a geographic surface by interpolating discrete observational data [1]. An X-ray spectrum is represented as a nonlinear function of X-ray energy. GP is a generalized linear model that can approximate such nonlinear spectral shapes by linear regression in feature space. GP predicts a spectrum by tuning the hyper-parameters by learning experimental data points, namely photon energy versus intensity. Moreover, both the expectation and variance of the prediction can be evaluated. Therefore, the predictive certainty is known and an experiment can be designed adaptively (i.e., sampling new data points based on the variance).

We used an experimental XMCD spectrum to assess the applicability of GP modeling. SmM₄₅ XMCD and XAS spectra of SmCo₅, a typical permanent-magnet material, were measured using a scanning transmission X-ray microscope (STXM) at the BL-13A of the Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Japan [2]. Details of the STXM experiment are described in the literature [3].

Figure 1 shows a flowchart of the adaptive design of the XMCD spectroscopy experiment, in which one can evaluate magnetic moments in a sampling-by-sampling regime. First, initial data points are sampled to obtain an experimental spectrum as the training data. Next, a spectrum is predicted by GP modeling fitted to the training data. Then, magnetic moments are evaluated from the predicted spectra. The experiment is stopped if the values of the magnetic moments satisfy the convergence criterion. Otherwise, new data points are sampled and the spectrum is predicted again. We examined three methods for the selection of new sampling data points. (1) Sample the data point with maximum variance (max. var.) of the predicted spectrum, (2) random sampling, and (3) random sampling weighted with variance (i.e., a data point with large variance has a high possibility of being sampled). Hereafter, this sampling method is called “weighted sampling.” Note that random sampling and weighted sampling were examined 50 times with different random numbers and averaged for all examinations.

Figure 2 shows the results of the adaptive design of the XMCD spectroscopy experiment. Typical XMCD spectra predicted by the GP model are shown in Fig. 2(a)–(d). The initial 30 data points were extracted from the experimental XMCD spectrum. Variances in the predicted spectra (red solid curves) became large among the observed data points. By increasing the number of observed data points, the total variance of the predicted spectra decreased and the spectral shape of the predicted spectrum became similar to that of the experimental (true) spectrum. Figure 2(e) shows the orbital magnetic moment mₒ, evaluated from the predicted spectrum plotted as a function of
the total number of data points with different sampling methods. True values for the magnetic moments and the ±5% errors are indicated by black solid and dashed lines, respectively. The orbital magnetic moment converged to the true value at around 40 total data points with maximum variance sampling. Random sampling showed poor convergence to the true value even with 100 data points. Weighted sampling behaved halfway between maximum variance sampling and random sampling, and showed good convergence to the true value. Figure 2(f) shows the total number of data points for the various sampling methods to satisfy the convergence criterion. All sampling methods satisfied the convergence criterion at around 50 points.

In conclusion, we demonstrated the adaptive design of an XMCD spectroscopy experiment with GP modeling. GP was found to predict the nonlinear spectral shapes of the XMCD spectrum successfully. Magnetic moments could be evaluated from the predicted spectra with the required level of accuracy. The present method reduces the total number of data points for measurement as well as the time and cost of an XMCD spectroscopy experiment. This method has potential applicability to various spectroscopies. It drastically reduces the measurement time for point-by-point measurements, such as scanning transmission X-ray microscopy with scanning energy points around absorption edges.

Acknowledgments

Part of this work was supported by the Elements Strategy Initiative Center for Magnetic Materials (ESICMM) under the outsourcing project of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This work was supported in part by the “Materials Research by Information Integration” Initiative (MFII) project of the Support Program for Starting Up Innovation Hub from the Japan Science and Technology Agency (JST). This work was supported by JSPS KAKENHI Grant Numbers 15K17458, 16K16108, and 25120011. The authors thank Shin-Etsu Chemical Co., Ltd., for providing SmCo5 material. The STXM experiment was performed with the approval of the Photon Factory Program Advisory Committee (Proposal No. 2015MP004).

References

Electrides are crystals with cavity-trapped electrons serving as anions. An inorganic electride \([\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(e^-)^4\) synthesized by Hosono et al. [1] in 2003 by using a main-group oxide \(12\text{CaO}\cdot7\text{Al}_2\text{O}_3\) (C12A7) is found to be stable in air up to 400°C, in sharp contrast to organic ones synthesized to date, which have been reported to be sensitive to air and moisture and decompose above roughly -40°C. As such, there has been less active investigation of organic electrides thus far, even though they are expected to exhibit various interesting physical and chemical properties arising from the presence of localized electrons. By contrast, C12A7:e\(^-\) is found to enhance the catalytic activity of Ru for NH\(_3\) synthesis significantly when loaded on C12A7:e\(^-\) [2]. Interestingly, the poisoning of Ru surfaces by H adatoms is reported to be suppressed effectively because C12A7:e\(^-\) is capable of storing hydrogen reversibly in the form of H\(^-\) anions. Therefore, knowledge about the microscopic behavior of hydride H\(^-\) included in the cages of C12A7 systems would be useful for developing high-performance hydrogen-storage materials aimed at their practical use.

We investigated the behavior of hydrides in nanoporous C12A7:H\(^-\) by using Born–Oppenheimer (BO)-based centroid molecular dynamics (CMD), in which the quantum nature of nuclei is accounted for explicitly by using the path integral technique. As shown in Fig. 1, the system we employed includes 24 Ca\(^{2+}\), 28 Al\(^{3+}\), 64 O\(^{2-}\), and 4 H\(^-\) ions in a cubic unit cell of side \(L = 11.99\ \text{Å}\), which corresponds to C12A7:H\(^-\) with the maximum concentration of H\(^-\). The distribution of H\(^-\) anions contained in the cages of our C12A7:H\(^-\), obtained at 300 and 100 K from our BO-CMD simulations, is shown in Fig. 2(a) and (c), respectively. For comparison, the corresponding distributions obtained by performing BO-MD simulations, in which the quantum nature of nuclei is ignored, are also shown in Fig. 2. In both BO-CMD and -MD results, 4 H\(^-\) anions are found to be widely distributed at 300 K in a similar fashion in the cages, as shown in Fig. 2(a) and (b), respectively, indicating that the thermal fluctuations dominate the quantum ones at 300 K. By contrast, the considerable difference of the H\(^-\) distributions between the BO-CMD and -MD results is clearly visible at 100 K, as shown in Fig. 2(c) and (d), respectively. This suggests that the behavior of hydrides in C12A7:H\(^-\) is governed mainly by the quantum nature of nuclei at such low temperatures.

Figure 3 shows the computed full width at half maximum (FWHM) of the distributions of H\(^-\) and D\(^-\) in our C12A7 systems. The approximate size of the cage constituting a C12A7 framework is roughly 1.2 Å smaller in radius along the \(S_4\) symmetry axis than that perpendicular to it. Reflecting this anisotropic shape of the cage containing an anion, the computed FWHM values of the distribution of the centroids along the \(S_4\) axis (denoted as \(\rho_{||}(H^-)\)) obtained from our BO-CMD simulations are found to remain almost constant throughout the temperatures we considered, whereas those of the corresponding distribution perpendicular to the \(S_4\) axis (denoted as \(\rho_{\perp}(H^-)\)) are...
shown to decrease linearly with decreasing temperature. For D\(^-\),
the computed FWHM values show similar trends to the corresponding values for H\(^-\); however, we find that they are systematically smaller by 0.04 (0.07) Å for ρ || (D\(^-\)) (ρ \(\perp\) (D\(^-\))) than those for ρ || (H\(^-\)) (ρ \(\perp\) (H\(^-\))). By contrast, the BO-MD results do not show such systematic difference in the distributions of H\(^-\) and D\(^-\) anions, which is certainly due to the absence of zero-point vibrations in the BO-MD approach.

Figure 4 shows our computed infrared (IR) absorption ((a) and (b)) and Raman scattering ((c) and (d)) spectra for C12A7:H\(^-\) ((a) and (c)) and C12A7:D\(^-\) ((b) and (d)). For C12A7:H\(^-\), both IR and Raman spectra show rather small features attributed to the vibration of H\(^-\) at 600 and 950 cm\(^{-1}\). Their tiny intensity found in our computed spectra for C12A7:H\(^-\) indicates that the dephasing of the vibration of H\(^-\) anions occurs in a very short time because of the strong quantum nature of the H nuclei. By contrast, for C12A7:D\(^-\), we find that the intensities of some peaks in the IR and Raman spectra, associated with the vibration of D\(^-\) located at around 300, 450, and 700 cm\(^{-1}\), are reduced appreciably compared to those for C12A7:H\(^-\). This indicates that the vibration modes of D\(^-\) anions, which have considerably smaller amplitude on average than those of H\(^-\) anions, behave as part of the phonons, in which they oscillate in phase with Ca\(^{2+}\) ions for the modes of ~300 cm\(^{-1}\) and with Al\(^{3+}\) ions for the modes of ~450 and ~700 cm\(^{-1}\). Therefore, our detailed analyses of the vibrational states reveal that the vibrations of H\(^-\) are virtually independent of each other, while those of D\(^-\) are highly collective, thereby resulting in the non-trivial isotope effects, which are suggested to be detectable using IR absorption and Raman scattering spectroscopy.

Acknowledgment

The numerical calculations were performed using the SGI ICE X supercomputer at the Japan Atomic Energy Agency (JAEA).

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