PROCEEDINGS OF SCIENCE

Development of a Polarized Lanthanum Target with Perovskite Crystals

M. Iinuma,[a,*] R. Akao,[b] M. Fujita,[c] I. Ide,[d] Y. Ikeda,[c] T. Iwata,[b] S. Kawamura,[d] M. Kitaguchi,[d] H. Kohri,[e] S. Kudo,[d] Y. Miyachi,[b] T. Nambu,[d] T. Okudaira,[d] M. Okuizumi,[d] H. M. Shimizu,[d] S. Takada,[c] T. Taniguchi[c] and the NOPTREX collaboration

[a] *Hiroshima University, Higashi-hiroshima, Hiroshima, 739-8530, Japan*
[b] *Yamagata University, Yamagata 990-8560, Japan*
[c] *Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[d] *Nagoya University, Nagoya 464-8602, Japan*
[e] *Research Center of Nuclear Physics, Osaka University, Ibaraki 567-0047, Japan*

E-mail: iinuma@hiroshima-u.ac.jp

It is widely known that a solid polarized target is a powerful device in research of spin physics, such as investigations of spin structure of nucleons, spin correlation in nuclear reactions, and precise measurements of discrete symmetries. In practical beam experiments, the solid polarized targets are limited to protons and deuterons since a relaxation time of nuclei with a large quadrupole moment is very short under a typical magnitude of external magnetic field. A possible method for overcoming such a problem is to perform the Dynamic Nuclear Polarization(DNP) with perovskite crystals, which is expected as a new way for opening up further possibilities in spin physics. The NOPTREX collaboration applies this method for the development of a polarized lanthanum (^{139}La) target, which is a core device for discovery of Time-reversal violating effects with a slow neutron. We will introduce a basic concept and some features of the method, and also show the current status on Research and Development(R&D) of the polarized ^{139}La target in the NOPTREX project.

20th International Workshop on Polarized Source, Targets, and Polarimetry (PSTP2024)
22-27 September, 2024
Jefferson Lab, Newport News, VA

*Speaker

PoS(PSTP2024)002

1. Introduction

In particle and nuclear physics experiments, a polarized solid target is a significant tool in terms of availability of nuclear spins as an additional degree of freedom, and is practically used for investigation of spin structure of nucleons, spin correlation in nuclear reactions, precise measurements of discrete symmetries, etc.[1]. Thanks to cryogenic and microwave technologies and understanding of materials, some excellent targets, such as ammonia, LiH, have been developed based on the Dynamic Nuclear Polarization(DNP) technique[2]. However, such practical targets are still limited to protons and deuterons. One of the main reasons is that the spin-lattice relaxation time(T_1) of a nucleus with a large quadrupole moment is very short under a typical magnitude of external magnetic field in beam experiments due to a coupling between the quadrupole moment and the surrounding electric field gradient, where the quadrupole moment of many nuclei is typically higher compared to the deuteron. To overcome this problem, a possible way is to perform the DNP with a perovskite crystal because the local charge distribution under its structural symmetry produces the preferred electric field gradient to suppress the extra relaxation process. This method has potential for realizing practical polarized targets with a high quadrupole moment.

On the other hand, a polarized Lanthanum (^{139}La, $I = 7/2$) target is very interesting because this is a core device for exploring time-reversal violating effects with slow neutron transmission. It is well known that large enhancements of the parity non-conservation effect (PNC) in the neutron-induced compound state have been observed in many nuclei approximately $10^2 - 10^6$ larger compared to proton-proton scattering. Particularly, the ^{139}La shows the enhancement of about 10^6 in the p-wave resonance(E=0.74 eV) with a polarized neutron beam, which is the biggest enhancement in all past observations. Furthermore, recent experiments have shown that the enhancement mechanism is also expected for the T-violating effects by measuring an angular distribution of emitted gamma ray[3, 4]. For bringing a sensitivity to the T-violation into this system, it is necessary to polarize nuclear spins in targets, as well as a polarizer and an analyzer for the neutron beam. Although the quadrupole moment of ^{139}La nuclei is approximately two order higher than that of the deuteron, a single crystal of Nd^{3+}:$LaAlO_3$, where Neodymium (Nd) ions are doped in a perovskite crystal of $LaAlO_3$ as paramagnetic dopants, has shown about 50 % polarization of ^{139}La less than 0.3 K in 2.3 Tesla based on the conventional DNP technique[5]. This result has encouraged the NOPTREX collaboration to carry out the research and development(R & D) of the polarized ^{139} La target for the exploration of the enhancement-assisted T-violating effect. The R & D is also a great challenge in terms of impact on the realization of polarized targets of general nuclei because the magnitude of the quadrupole moment of ^{139} La is roughly middle in all nuclear species.

In actual T-violation search with ^{139}La nuclei, it is specifically required to keep high polarization in about 0.1 Tesla, which corresponds to a strength of the magnetic field for canceling out a systematic effect caused by the pseudomagnetic rotation of a neutron spin[6]. A typical way of solving the above problem is the spin-frozen operation[7], where the target spins are firstly polarized in a high magnetic field, such as 2.3 Tesla, and then the magnetic field is reduced to about 0.1 Tesla after cooling down the target to an ultra-low temperature. In this scenario, since a time for beam irradiation is eventually limited to the T_1 in about 0.1 Tesla, it is very significant to study on the relaxation of ^{139}La in the Nd^{3+}:$LaAlO_3$ crystals in the low magnetic field. In the circumstance where the additional relaxation caused by the quadrupole moment is not dominant and crystalline

quality of the target is high, a concentration of the Nd ions is essential for the T_1 because lower Nd concentration generally makes the T_1 longer. Meanwhile, lower concentration undoubtedly reduces the efficiency of the DNP. Therefore, the optimization of the Nd concentration is necessary with high-crystalline samples with various concentration of the Nd ions. The important issues for this task are to establish a crystal growth method to prepare good samples, to make simple DNP tests with them, and to evaluate them in terms of the T_1 and a polarization in saturation for feedback to the crystal growth.

In this report, we introduce a basic concept and some features of the method, and also show the current status on the R&D of the polarized ^{139}La target in the NOPTREX project.

2. DNP with the perovskite crystal

2.1 Relaxation process

In the typical polarized target, such as protons and deuterons, the dominant relaxation process is induced by the dipole-dipole interaction between an electronic magnetic moment and a nuclear magnetic moment as shown in Fig. 1(a) [8]. Although the high polarization of electron spins, which are put into target materials as paramagnetic dopants in the DNP, is almost constant in thermal equilibrium, the direction of each electron spin is always fluctuating because of lattice vibrations. Since the electron spins are constantly coupled to surrounding nuclear spins by the dipole-dipole interaction, their thermal fluctuation is responsible for the relaxation of nuclear spins to the thermal state. Significantly, larger concentration of electrons accelerates the decay of nuclear polarization through this process. Therefore, the relaxation time T_1 is controllable by adjusting the concentration of the paramagnetic dopants. It should be noted that lower concentration of the paramagnetic dopants reduces the efficiency of the DNP because they also have a role of the seed of the nuclear polarization. As the result, it is necessary to optimize the concentration of the dopants for obtaining the maximum polarization in the DNP.

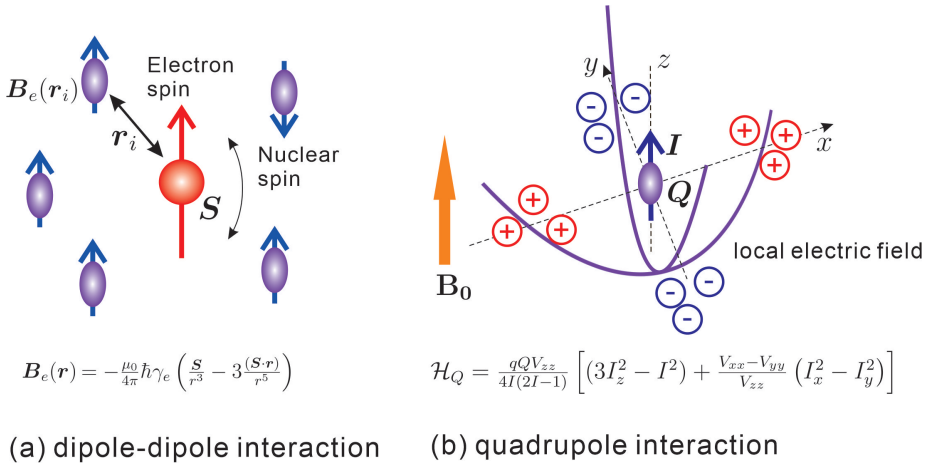

Figure 1: Dominant relaxation process. (a) is by the dipole-dipole interaction and (b) by the quadrupole interaction.

On the other hand, the relaxation process in nuclei with the quadrupole moment includes an additional process as shown in Fig. 1(b), which is induced by the quadrupole interaction to the

gradient of surrounding electric field. One explainable cause is the thermal fluctuation of the local electric field, which is produced by the lattice. However, the dominant process of the depolarization is in the interaction itself, which can be expressed as,

$$\hat{H}_Q = \frac{e^2qQ}{4I(2I-1)}\left[3\hat{I}_z^2 - \hat{I}^2 + \frac{\eta}{2}(\hat{I}_+^2 + \hat{I}_-^2)\right], \tag{1}$$

where $\hat{I}_\pm = \hat{I}_x \pm i\hat{I}_y$ are raising and lowering operators, $eq = V_{zz}$ shows the field gradient along the Z direction, $\eta = (V_{xx} - V_{yy})/V_{zz}$ is an asymmetry parameter of indicating the field gradient on the XY surface, and Q is the quadruple moment. This interaction obviously induces a transition between two nearby Zeeman sublevels of the nuclear spins($I \neq 1/2$) in applying the magnetic field along the Z direction, and consequently causes the depolarization if the η is not zero. For preventing this process, it is required to control the local electric field surrounding nuclear spins to satisfy the condition of $\eta = 0$.

2.2 Features of $LaAlO_3$ crystals

A Nd^{3+}:$LaAlO_3$ crystal is structurally identical to a perovskite crystal $LaAlO_3$, as shown in Fig. 2, where a little amount of La^{3+} ions are replaced with Nd^{3+} ions having the role as the paramagnetic dopants in the DNP. The crystal structure is cubic above 813 K. At 813 K, the cubic-rhombohedral

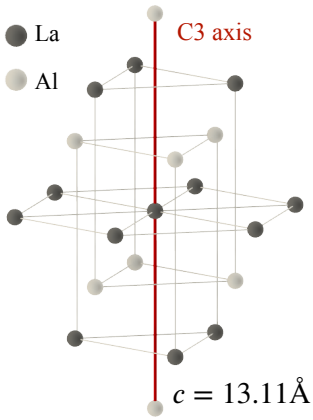

Figure 2: Crystal structure of a single crystal of $LaAlO_3$

phase transition occurs[9], and below that, the distortion of the crystal eventually provides the rhombohedral perovskite structure and naturally forms twinning domains. This crystal structure has two remarkable features as follows[10].

- All sites of La are magnetically equivalent in one domain
- The La site has the threefold rotational symmetry(C_3)

These features are quite favorable for the La DNP. The first feature makes the microwave-transition frequency equal among all Nd ions because they enter into the La sites. As the result, a linewidth in the Electron Paramagnetic Resonance(EPR) becomes quite narrow, where narrower

EPR linewidth increases the efficiency of the polarization transfer in the DNP. Practically, the reference[10] has observed the EPR linewidth of 0.0006 Tesla, which is almost independent of the strength of the magnetic field and explained from the superhyperfine interaction to nuclear spins of surrounding Al($I = 5/2$).

On the other hand, the second feature is more important from the perspective of the relaxation process because it ensures an axial symmetry of the electric field gradient in all La sites about the C_3 rotational axis. As the result, the $\eta = 0$ in all La sites is satisfied on the C_3 axis. In applying the magnetic field along the C_3 axis, since the transition between two Zeeman sublevels of the La spins($I = 7/2$) is not induced, the quadrupole interaction does not cause the depolarization even in a low magnetic field. As the result, the spin-lattice relaxation dominantly occurs via the dipole-dipole interaction to various paramagnetic impurities, such as vacancy-type defect, unwanted contamination, and the Nd ions, as the similar to the typical polarized target.

2.3 Issues for realization of the polarized target

In the past, two DNP experiments with an identical Nd^{3+}:$LaAlO_3$ have been carried out under different conditions, which Nd concentration is 0.03 mol%. The first experiment has successfully observed the 20 % polarization of La at 1.5 K and 2.3 Tesla[11] and then, the second experiment has achieved about 50 % polarization less than 0.3 K and at 2.3 Tesla[5]. These achievements show a high potentiality of the Nd^{3+}:$LaAlO_3$ crystal as the polarized La target, but the spin-frozen target for the T-violation search requires that the absolute T_1 is sufficiently long in approximately 0.1 Tesla. Therefore, it is necessary to investigate the T_1 in such a magnetic field and to overcome the typical relaxation problem if the T_1 is too short.

We have measured the T_1 of a commercial crystal with 0.03 mol% under various conditions in the Research Center of Nuclear Physics(RCNP), Osaka University, Japan and estimated the T_1 at 0.1 Tesla and 0.1 K by extrapolating these results[12], where the temperature of 0.1 K is achievable with a dilution cryogenic system. The result is

$$T_1(0.1\ \text{Tesla}, 0.1\ \text{K}) \geq 1\text{hour} \tag{2}$$

This result has clarified two points as follows: one is that the T_1 is likely to be different depending on the crystalline quality, and the other is that the optimization of the Nd concentration is necessary. Actually, the crystal showing the above result has not been confirmed whether the polarization is enhanced or not by the DNP. Meanwhile, the reduction of the Nd concentration certainly makes the T_1 longer although it also decreases the efficiency of the polarization transfer in the DNP. Therefore, a next issue is to find an optimal concentration of the Nd ions, particularly in the region of less than 0.03 mol%, with highly-crystalline samples, which should be confirmed on the enhancement of the polarization by the DNP.

3. Current status

3.1 Combination of crystal growth and DNP test

For optimizing the Nd concentration, we have established a system combining a crystal growth based on the Floating Zone(FZ) method and the DNP test in 1.3 K and 2.3 Tesla by using the glass dewar as shown in Fig. 3[13].

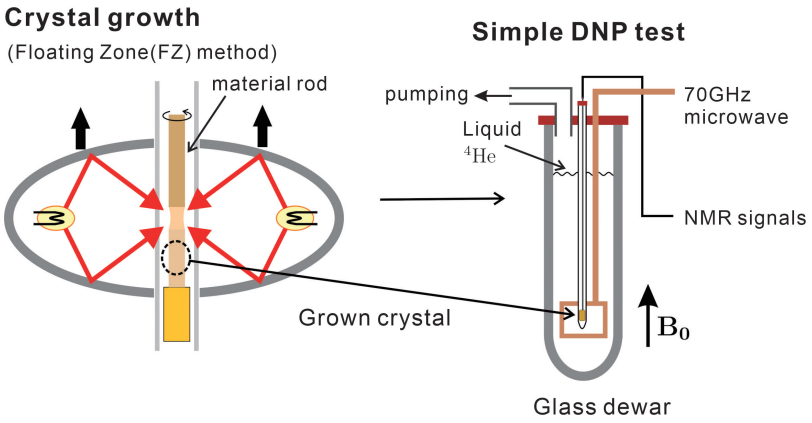

Figure 3: System combining the crystal growth and the DNP test. The crystal growth based on the Floating Zone(FZ) method is implemented by ourselves in IMR, Tohoku University, Japan. We test the grown crystals by actually performing the DNP in 1.3 K and 2.3 Tesla with the glass dewar in Yamagata University, Japan.

The important points on the crystal growth in this system are,

- Growth of the crystals showing sufficient effectiveness of the DNP
- Contamination control of unexpected impurities in whole process
- Precise control of the amount of Nd ions in preparation of material rod

The FZ method is adaptable to grow appropriate crystals flexibly at low cost although it is not suitable for growing a large size of crystal, such as 15 mm cubic. Further, the contamination control of unexpected impurities is relatively easier compared to other methods because a crucible is not used, which typically causes the contamination of paramagnetic impurities including Ir, W, and Mo, into the crystals. In the past, xenon lamps has been used for the FZ apparatus because of high melting temperature (2100 °C) of pure $LaAlO_3$. In contrast, for low cost, we have adopted halogen lamps for the first time and found optimal conditions under the use of this apparatus, in IMR, Tohoku University, Japan[13].

Raw materials used for the material rod, which diameter is about 5 mm, are $La(OH)_3$ (4N), Al_2O_3 (4N) and Nd_2O_3, where the "4N" indicates a guaranteed value of the purity of material, ≥99.99 %. Crystalline part of about 40 mm is produced in the material rod after process of the crystal growth. The crystal axis (one selected C_3 axis in four domains) is controlled to be parallel to the cylindrical axis of the material rod. Sample pieces are cut from the material rod and roughly selected through the evaluations with the X-ray Laue, the ESR, and the high-resolution NMR. For the first sample with 0.05 mol%, for example, the CW-ESR with 9.5 GHz microwave at 10 K has showed that the primary domain has the effective g-factor of 2.12 and the ESR linewidth at full-width-half maximum of 0.0006 Tesla, which are comparable with the 0.03 mol% crystal used in the previous DNP experiments [10, 14].

On the DNP tests of the crystals grown by ourselves, it is preferable to flexibly implement with a simple DNP apparatus. We have used the DNP apparatus based on the glass dewar in Yamagata University, which provides the DNP environment of 2.3 T and 1.3 K[15]. The samples were fixed inside of the copper box and cooled down by pumping the vapor of the liquid ^{4}He in the glass dewar.

The microwave was irradiated in the copper box, where the frequency was approximately 70 GHz and the initial power from the oscillator was about 0.2 W. The NMR signals for monitoring the enhancement of polarization were detected by sweeping the RF frequency with the continuous wave (CW) NMR system, which can be confirmed in online by simply comparing the signals after the DNP to the ones at thermal equilibrium. The NMR frequency was tuned for the detection of both ^{139}La and ^{27}Al NMR signals, which were practically observed by adjusting the magnetic field. The samples were aligned for the C_3 axis of the primary domain to be parallel to the external magnetic field B_0.

In this cryogenic system, the time available for the DNP test is limited to about 6 hours by the amount of Liquid ^{4}He stored in the dewar[13, 15]. Such a time restriction does not bring major problems only for selecting better condition among the grown crystals.

3.2 Current summary about the Nd optimization

In the DNP tests with grown crystals, the first concentration was 0.05 mol%[13], followed by 0.01 mol%[15]. Combining the present results with the past ones[11], the dependence on the Nd concentration is summarized as the table1.

Nd concentration	DNP condition	La	T_1	Al	growth
0.3 mol% [11]	2.3 T, 1.5 K	-	-	-	commercial
0.05 mol% [13]	2.3 T, 1.3 K	0.27 %	15 min.	0.28 %	ourselves
0.03 mol% [11]	2.3 T, 1.5 K	20 %	80 min.	-	commercial
0.01 mol% [15]	2.3 T, 1.3 K	> 20 %	> 120 min.		ourselves
0.003 mol% [11]	2.3 T, 1.5 K	-	-	-	commercial

Table 1: Summary of the DNP results about the Nd concentration

In the 0.01 mol% crystal, we have not been able to observe the saturation of polarization or to obtain a complete decay curve of the polarization due to the restriction of the measurable time. The T_1 of the 0.01 mol% crystal in this table is the estimation from the buildup curve assuming that the T_1 is longer than the buildup time[15]. In the 0.003 mol% concentration, there have been no experiments of observing the polarization enhancement. This level of the concentration is likely to be comparable to the one of unwanted impurities. Therefore, the Nd concentration of about 0.003 mol% may be the lower limit if commercially available raw materials are used without further purification.

Before these experiments, the 0.03 mol% concentration was thought to be the best. These studies show that the Nd concentration of 0.01 mol% is better than 0.03 mol% in terms of both of longer T_1 and higher saturated polarization. Further, the latest experiment with the 2 W microwave oscillator has demonstrated surprisingly high polarization of ^{27}Al($I = 5/2$) in the environment of 1.3 K and 2.3 Tesla, which is inferable as more than 30 % from comparison with the enhanced NMR spectrum obtained in the past PSI experiments[5]. Taking into account of this result also, we can conclude that the 0.01 mol% crystal is the best at present. These studies also show that we technically achieve the precise control to distinguish between 0.03 mol% and 0.01 mol% on the Nd concentration in the process of the crystal growth.

For checking the feasibility as the spin-frozen target and seeking better target, we need to tackle two following issues: one is the estimation of the T_1 of the 0.01 mol% crystal in 0.1 Tesla and 0.1 K, the other is further optimization of the Nd concentration in the region less than 0.01 mol%. It is also an important issue to evaluate the actual concentration of the Nd ions and the contamination of unwanted impurities in grown crystals by making an elemental analysis.

4. Summary

The DNP with perovskite crystals has a potential as a powerful technique for realizing the polarized target of nuclei with a large quadrupole moment, which is expected to open further possibilities in spin physics. The extra relaxation process for nuclear spins($I \neq 1/2$) can be suppressed due to the symmetry of the local electric field surrounding the nucleus. On the other hand, the polarized target of ^{139}La nuclei is attractive to both of the application to the T-violation search with a slow neutron and the impact to feasibility of the polarized target except protons and deuterons. The perovskite crystal Nd^{3+}:$LaAlO_3$ crystal, is promising for the polarized La target because the feature of this crystal brings great advantages to the La DNP.

For the realization of the T-violation experiment, the most important issue is to optimize the concentration of the Nd ions behaving as paramagnetic dopants. For this purpose, we have established the system comprised of the crystal growth based on the Floating Zone method and the simple DNP tests in 1.3 K and 2.3 Tesla. Two crystals with 0.05 mol% and 0.01 mol% have been grown by ourselves in IMR, Tohoku University and tested by performing the DNP in Yamagata University. As the result, the 0.01 mol% crystal has shown longer T_1 and higher saturated polarization compared to the 0.03 mol% crystal, which was thought to be the best.

In conclusion, the 0.01 mol% crystal is the best at present. The remaining issues are the estimation of the T_1 in 0.1 Tesla and 0.1 K, which are required for the T-violation experiment, and the further optimization in the region less than 0.01 mol%. In parallel, we are also planning to apply the 0.01 mol% crystal to the polarized La target in experiment as the first step toward the T-violation search.

5. Acknowledgements

The research on development of the polarized La target was performed under the RCNP project “Development of polarized target for new physics search via T-violation”, RCNP Collaboration Research Network program(Project No. COREnet-026), and partially-approved RCNP project Category I "Development of various polarized nuclear targets with dynamic and static nuclear polarizations" of the Research Center of Nuclear Physics, Osaka University. The material research was performed under the GIMRT Program(Proposal No. 19K0081, 20K0018), the inter-university cooperative research program of the Cooperative Research and Development Center for Advanced Materials(Proposal No.18G0034, 19G0037, 202012-CRKEQ-0015, 202112-CRKEQ-0032, 202212-CRKEQ-0044) and the inter-university cooperative research program of the Center of Neutron Science for Advanced Materials(Proposal No. 20N0002, 202012-CNKXX-0001, 202112-CNKXX-0009, 202212-CNKXX-0024), Institute for Materials Research, Tohoku University. The EPR experiments were conducted with H. Mino, Nagoya University

References

[1] For example, D. G. Crabb and W. Meyer, Solid Polarized Targets for Nuclear and Particle Physics Experiments, *Anuu. Rev. Nucl. Part. Sci* **47**, 67-109, 1997.

[2] For example, T. O. Niinikoski, *The Physics of Polarized Targets*, Cambridge University Press, 2020.

[3] T. Okudaira, et al., *Phys. Rev. C* **97**, 034622, 2018.

[4] T. Yamamoto, et al., *Phys. Rev. C* **101**, 064624, 2020.

[5] P. Hautle and M. Iinuma, *Nucl. Instrum. Methods Phys. Res. A* **440**, 638-642, 2000.

[6] V. Gudkov and H. M. Shimizu, *Phys. Rev. C* **95**, 045501, 2017.

[7] T. O. Niinikoski and F. Udo, *Nucl. Instrum. Meth.* **134**, 219, 1976.

[8] A. Abragam and M Goldman *Nuclear magnetism: order and disorder*, Oxford University Press, 1982.

[9] S. A. Hayward, et al. *Phys. Rev. B* **72**, 054110, 2005.

[10] Y. Takahashi, et al., *Nucl. Instrum. Methods Phys. Res. A* **336**, 583-586, 1993.

[11] T. Maekawa, et al., *Nucl. Instrum. Methods Phys. Res. A* **366**, 115-119, 1995.

[12] K. Ishizaki, et al., *Nucl. Instrum. Methods Phys. Res. A* **1020**, 165845, 2021.

[13] K. Ishizaki, et al., *Rev. Sci. Instrum.* **95**, 063301, 2024.

[14] K. Ishizaki, et al., *PoS(PSTP2019)*, 61, 2019.

[15] I. Ide, et al., *PoS(PSTP2022)*, 038, 2023.