Matter and
Radiation at Extremes REVIEW scitation.org/journal/mre

Pulsed-field nuclear magnetic resonance: Status and prospects

Cite as: Matter Radiat. Extremes 6, 024201 (2021); doi: 10.1063/5.0040208
Submitted: 11 December 2020 • Accepted: 31 January 2021 •
Published Online: 25 February 2021

View Online Export Citation CrossMark

Qinying Liu,[1,2] Shiyu Liu,[1] Yongkang Luo,[1] and Xiaotao Han[1,2,a)]

AFFILIATIONS

[1] Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology, Wuhan 430074, China
[2] State Key Laboratory of Advanced Electromagnetic Engineering and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

[a)] **Author to whom correspondence should be addressed:** xthan@mail.hust.edu.cn

ABSTRACT

High-magnetic-field nuclear magnetic resonance (NMR) has manifested itself as an indispensable tool in modern scientific research in the fields of physics, chemistry, materials science, biology, and medicine, among others, owing to its great advantages in both measurement sensitivity and quantum controllability. At present, the use of pulsed fields is the only controllable and nondestructive way to generate high magnetic fields of up to 100 T. NMR combined with pulsed fields is therefore considered to have immense potential for application in multiple scientific and technical disciplines. Irrespective of the paramount technical challenges, including short duration of the pulsed fields, unstable plateaus, and poor field homogeneity and reproducibility, great progress has been made in a number of pulsed-field laboratories in Germany, France, and Japan. In this paper, we briefly review the status of the pulsed-field NMR technique, as well as its applications in multiple disciplines. We also discuss future trends with regard to the upgrading of pulsed-field NMR.

I. INTRODUCTION

Since Rabi invented the magnetic resonance method to study the nuclear magnetism of gaseous atoms in 1944, research achievements related to nuclear magnetic resonance (NMR) have won five Nobel Prizes for work in areas including nuclear spin, spectral transformation, and magnetic resonance imaging (MRI): two in Physics, two in Chemistry, and one in Medicine. The essential characteristic of NMR is that it opens the door to direct study of the magnetic moments of nucleons, and can measure the magnetic properties of an atomic nucleus whose mass, in the case of hydrogen, is just 1840 times the mass of an electron. Techniques based on NMR are therefore widely used as research tools in several areas of physics, chemistry, materials science, and biomedicine. Much effort has been dedicated to the development of NMR techniques, with several breakthroughs occurring in the past few decades that have made NMR one of the most widely used experimental methods.

In the past, there was a general consensus that it was very difficult to perform NMR experiments in an unsteady magnetic field, especially a pulsed field. However, with the development of NMR technology, many amazing nuclear magnetic phenomena have been found in unstable magnetic fields such as the high magnetic fields provided by hybrid magnets.[1–3] The discovery of such field-induced exotic behavior under extreme conditions has motivated attempts to further increase the background field intensity and explore ways to apply NMR techniques in higher pulsed magnetic fields, bringing pulsed-magnetic-field NMR (PF-NMR) to center stage in recent years. The use of PF-NMR promises to be of great value in many ways, including the following.

First, PF-NMR should allow improvements in the detection signal-to-noise ratio (SNR). Although NMR has precise site-selection properties, its inherent low signal strength has always been a notorious disadvantage. With the increasing demand for high-throughput and multidimensional studies, in order to improve the SNR, it is necessary to perform multiple signal sampling, which results in massive amounts of data, and the time required has become a major constraint on applications.[4] The SNR of an NMR spectrogram has a power-law dependence on the magnetic field intensity:

$$\mathrm{SNR} \propto \gamma f^{3/2} \propto \gamma^{5/2} B^{3/2}, \tag{1}$$

where γ is the gyromagnetic ratio, f is the resonance frequency, and B is the intensity of the magnetic field. Therefore, to improve the SNR, the background magnetic field strength needs to be increased. However, permanent magnets, superconducting magnets, and hybrid magnets all have a critical temperature for operation and are all subject to deformation by electromagnetic forces. So far, the maximum magnetic field strength produced by superconducting magnets can only reach 32.35 T,[5] and that of hybrid magnets can only reach 45 T.[6,7]

For example, in the biological field, in order to ensure an acceptable SNR in existing MRI studies of macromolecules, multiple collections of data must be superimposed. The acquisition time can be reduced by the addition of a paramagnetic reagent as co-solute to shorten the relaxation time, by increasing the scanning speed, or by optimizing the filter performance to allow estimation of multiple samples at the same time; alternatively, the sample concentration can be increased to achieve high-throughput multidimensional NMR measurements.[8–11] Nevertheless, many problems remain, such as limited space for the arrangement of the probe terminals[12] and the large amounts of data that are acquired.[13] Much work has been devoted to these problems, but they have not been tackled at root. High-field NMR provides a fundamental approach to solving these problems. Increasing the background magnetic field will directly expand the range of energies corresponding to each energy level and enhance the resonance signal. In biological applications, on the one hand, a higher background field significantly enhances the SNR of the resonance signal, which reduces the time required for an experiment thus allowing study of the structure and dynamical changes of biological macromolecules with molecular weights up to several megadaltons. On the other hand, the Larmor resonance frequency becomes higher in an ultrahigh magnetic field, leading to higher resolution. More subtle chemical environmental changes can be distinguished, and the capability of NMR to recognize various groups of biological macromolecules can be increased.

Second, PF-NMR should allow the exploration of the peculiar physical properties of special systems that are far from the normal state under ultrahigh field strengths. NMR provides an effective method to directly detect the electron energy density, which defines the properties of materials. Therefore, it is a very important tool for exploring new phases and phenomena driven by magnetic fields. Moreover, a large number of experiments have shown that when the external magnetic field reaches a certain strength, some special phenomena that do not appear at low fields can be observed, such as the Wigner crystal state in low-dimensional quantum systems,[14] suppression of superconductivity,[15,16] the de Haas–van Alphen (dHvA) effect, the Shubnikov–de Haas (SdH) effect[17] in two-dimensional ultrathin materials,[18] topological materials,[19] and complex magnetic materials.[20,21] Where appropriate, PF-NMR can provide microscopic information at the nucleon level, as well as having great potential for the study of exotic field-induced effects in special systems.[22]

For example, in solid state physics, steady high-magnetic-field NMR at 33.5 T revealed the existence of a charge density wave (CDW) phase state in underdoped $p = 0.108$ and 0.12 samples of the well-known high-temperature superconductor $YBa_2Cu_3O_7$.[23] This proved the existence of orderly charges in high-T_c superconductors and indicated that the ordered state at the optimally doped quantum critical point may be this kind of CDW. However, no direct evidence could be obtained, because sample experiments close to the optimal doping must be carried out at higher magnetic fields, exceeding the design limit of known steady high-magnetic-field techniques.

Since the inherent SNR of the detection method is directly proportional to the 3/2 power of the background field strength, an increase in this strength can greatly improve the detection accuracy as well as significantly shortening the detection time. Furthermore, a high magnetic field can directly affect the electronic state and quantization of matter and significantly change the electronic structure, thus leading to special properties that would not appear under normal circumstances. This provides further motivation for the development of NMR techniques in higher magnetic fields, especially unstable pulsed fields.

The remainder of this paper is organized as follows. The current state of development of PF-NMR is described in Sec. II with regard to the pulsed magnets, high-frequency spectrometers, and signal processing strategies that are available. In Sec. III, prospective research applications of NMR in extremely strong magnetic fields are described. Then, in Sec. IV, considering these potential scenarios, the key technical problems faced in attempts to realize high-field and high-frequency NMR are analyzed. In Sec. V, a perspective for future developments of PF-NMR is presented. Finally, the paper is concluded in Sec. VI.

II. DEVELOPMENTAL STATUS

In an NMR experiment, Zeeman splitting is induced by applying a background magnetic field to nuclear spins, resulting in energy separation between sublevels. When the magnetic field is constant, according to the Boltzmann distribution law, the system will reach a certain thermal equilibrium. The population difference between the upper and lower spins is determined by the Boltzmann factor. At this time, the spectrometer emits a radio-frequency (RF) signal to cause the low-energy nucleus to transition to a high-energy level, with the original population distributions being destroyed. After removal of the RF field, the high-energy nucleus then spontaneously returns to the low-energy level, and the system re-establishes thermal equilibrium, i.e., relaxation occurs. In solids containing unpaired electrons, the relaxation stems from field fluctuations caused by pulsed electron moments. This can be regarded as an interactive electron–nuclear spin reversal scattering process, which keeps the angular momentum unchanged. The free induction decay (FID) signal is recorded by an *LC* coil around the sample. Through orthogonal frequency conversion, spectral transformation, and other signal processing methods, we can obtain nuclear spin information such as the Knight/chemical shift and relaxation time,[24] with the aim of analyzing the crystal structure and electronic state of the sample. To transplant the NMR method to higher magnetic fields, especially unstable strong fields such as pulsed fields, we need to ensure field stability, develop NMR spectrometers suitable for high fields and high frequency, and establish new algorithms for dynamic analysis of FID signals.

A. Early origin

In recent years, several high-field laboratories have carried out research on high-field NMR. The National High Magnetic Field Laboratory (NHMFL) in Florida started work very early on. In 2000, Murali's team pointed out that in order to take advantage of NMR in high magnetic fields, a magnetic field with high intensity, good spatial homogeneity, and temporal stability was needed. They demonstrated that in high-field NMR experiments, transient instability of steady-state magnets is mainly caused by ripples in the power supply and changes in the temperature of the cooling system. They therefore designed a de-ripple feedback coil and cooling system with an automatic correction mode that allowed them to obtain a 1.7 ppm line width in ^{2}D NMR at 24 T. A liquid sample was then spin-manipulated by the intermolecular zero-quantum-coherence (iZQC) method to reduce the influence of poor spatial homogeneity and temporal stability of the magnetic field on the spectrum, and they were thereby able to obtain the first high-resolution NMR spectrum up to 1 GHz.[25]

In 2002, NHMFL showed that phase noise results from the phase changes of continuously acquired NMR signals caused by an unstable external magnetic field, which leads to serious FID signal distortion during the signal averaging process.[1] With a reduced sample volume and the use of magic-angle spinning (MAS), NMR experiments on alumina mixtures were carried out for different field strengths, and the resonance spectra of a solid ^{27}Al sample were analyzed under a high field generated by a 40 T hybrid magnet (an 11 T superconducting magnet combined with a 29 T resistive magnet). As shown in Fig. 1, the spectral resolution gradually improved with increasing external magnetic field, and the resonance site was more clearly identified, thus solving the problem of spectral line aliasing of samples with strong quadrupole coupling in lower magnet fields. Further studies in the following years have shown that the NMR spectral resolution of resistive–superconducting hybrid magnets can be improved by ferromagnetic shimming, MAS, and heteronuclear phase correction, and the linewidth achieved under ideal conditions can be close to that achievable with superconducting magnets.[26] Other approaches, such as the use of pulse sequences that are not sensitive to magnetic field fluctuations to excite the sample, or feedback control systems that actively compensate for the shimming field to stabilize the magnetic flux, can significantly reduce the phase difference caused by magnetic field fluctuations between spin-echo signals.[27] These methods are expected to narrow the aliasing spectral peaks, allowing the observation of NMR phenomenon that cannot be detected with high resolution in low fields.

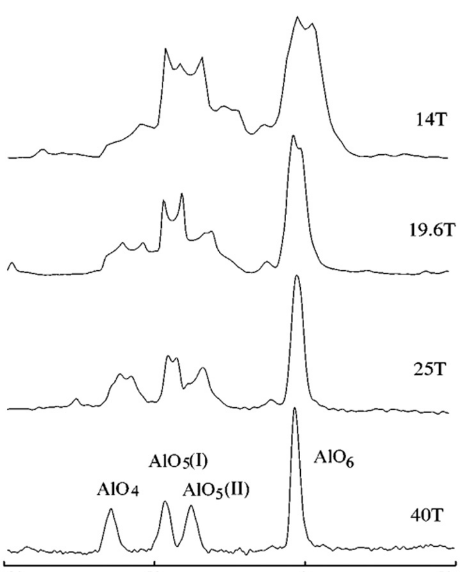

FIG. 1. ^{27}Al MAS-NMR spectra from 14 T to 40 T. Reprinted with permission from Gan *et al.*, J. Am. Chem. Soc. **124**, 5634 (2002). Copyright 2002 American Chemical Society.

At about the same time, in 2003, the Nijmegen High-Field Magnet Laboratory obtained FID spectral lines of ^{27}Al in a 24 T steady magnetic field by means of techniques including the use of a shimming insert, feedback of the power supply, and phase reference deconvolution.[28] The result indicated a clear nuclear quadrupole resonance (NQR). It is worth noting that the although the quadrupole interaction provides important structural information, it impairs spectral resolution and widens the central linewidth, and some nuclei will overflow outside the detection edge. This situation is called "NMR invisibility," which means that these nuclei in these special positions can only be observed under a higher magnetic field. Therefore, the results are consistent with NHMFL's inference, namely, that a high-field physical environment provides unique advantages for the NMR study of half-integer quadrupole nuclei (such as ^{27}Al, ^{23}Na, and ^{17}O).

In 2002, the National Institute for Materials Science (NIMS) conducted an NMR experiment in a 21.6 T superconducting magnetic field. In this study, although the magnetic field intensity was not very high, the problem of inhomogeneous broadening of spectral lines had already appeared. It was demonstrated in Ref. 29 that this problem can be alleviated by adding shimming coils, and FID results with a resolution of up to 4 Hz were obtained at a resonance frequency of 920 MHz. Although these pilot studies did not directly involve NMR experiments in a pulsed high magnetic field, they all reflected the trend of NMR experiments toward higher field strengths.

B. Development track

1. Budding technology

In 2003, the High Magnetic Field Laboratory Dresden (HLD) group proposed the concept of PF-NMR and conducted systematic experimental research,[30,31] including a feasibility analysis of magnetic field homogeneity, spectral resolution, SNR, and other factors. They carried out NMR experiments on ^{63}Cu under 12 T and 33 T pulsed high magnetic fields, and selected a time window near the peak to trigger the RF pulse at a fixed point, obtaining the results shown in Fig. 2.[32] Although there is a large ripple and the linewidth is not ideal, this was the first time that a useful FID signal had been collected in a pulsed field, and it marked the germination of PF-NMR technology. Some disadvantages were also noted, such as the strong time dependence of the pulsed field, the far lower spatial homogeneity than that available with commercial NMR superconducting magnetic fields, and the long cooling time. The experiments were optimized by reducing the sample volume to meet the requirements of higher magnetic field intensity, by broadening the instantaneous bandwidth of the RF signal to expand the scanning range, and by extending the pulse flattening time to ensure full polarization of the nuclear spin system.

The HLD group realized NMR of ^{2}D at a 58 T magnetic field in 2004,[33] and proposed a method of isotope comparison in the same year.[34] First, the ^{1}H ($\gamma = 42.5774$) resonance was excited in a steady-state field, and then ^{2}D ($\gamma = 6.5359$) was calibrated with gyromagnetic ratio multiples in the pulsed field. Taking advantage of the constant spin magnetic ratio of isotopes, the uncertainty caused by different electronic environments among elements was eliminated, and the

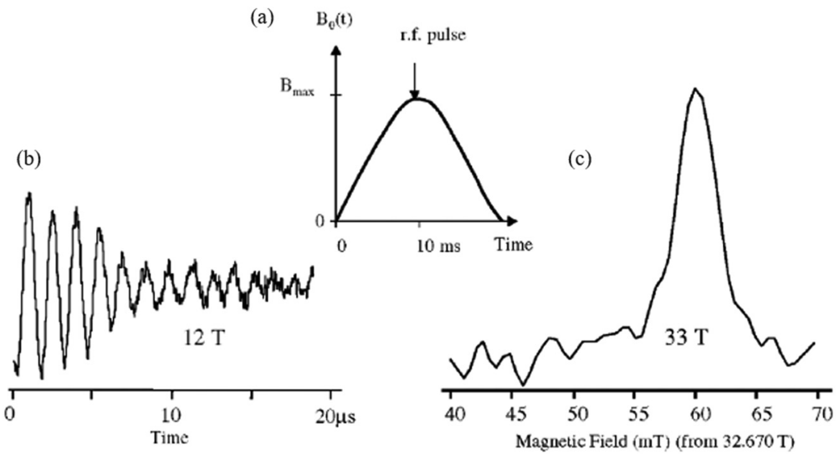

FIG. 2. (a) Background pulsed magnetic field. (b) ^{63}Cu FID at 12 T; (c) Fourier transform of ^{63}Cu FID at 33 T. Reprinted with permission from Haas *et al.*, J. Magn. Magn. Mater. **272-276**, e1623 (2004). Copyright 2004 Elsevier.

elements with low gyromagnetic ratio under a high pulsed field were measured. Then, by reducing the sample volume to adapt to the poorly homogeneous field, increasing the power amplifier magnification to narrow the bandwidth, and collecting multiple FID to reduce the signal uncertainty, the ^{1}H NMR spectrum was observed at frequencies of 1.3 GHz,[35] 2 GHz,[36] and 2.4 GHz.[37] NMR signal acquisition of elements with high gyromagnetic ratio was completed under a pulsed magnetic field of up to nearly 50 T, as shown in Fig. 3. Although the SNR is low in this stage, this is still strong evidence that NMR detection can be realized in a pulsed magnetic field.

These studies have indicated that PF-NMR represents a new stage in the development of NMR. It is significant not principally because of its ability to improve SNR and resolution, since measures such as increased flux, sample concentration, number of time average accumulations, and scanning speed can already do this. Rather, the field-induced collective electronic behavior that appears in ultrahigh magnetic fields, leading to exotic phase transitions and states of matter, can only be observed in a pulsed high magnetic field, and it is this that constitutes the unparalleled advantage of pulsed-field NMR over steady-field NMR.

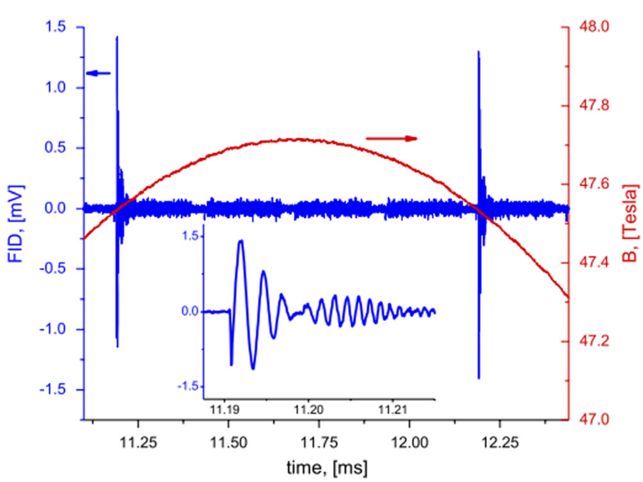

FIG. 3. ^{1}H FID under a 50 T pulsed high magnetic field. Reprinted with permission from Haas *et al.*, Solid State Nucl. Magn. Reson. **28**, 64 (2005). Copyright 2005 Elsevier.

2. Further studies

The years 2007–2016 represented the peak of PF-NMR development. Research teams from various institutions continuously optimized the relevant techniques. On the one hand, the background field conditions were improved through means such as spectrometer upgrades and magnet optimization, while methods such as magnetic field time-dependent interlocking FID phase, frequency-domain deconvolution, and signal normalization averaging were incorporated into algorithms to improve the quality of spectral analysis.

In terms of spectrometer development, in 2009, the Zheng team at Okayama University, using a home-built phase-coherent NMR spectrometer, obtained a ^{59}Co NMR shift[38] that was consistent with the 8 T steady-state field results in Ref. 39 and a peak width that was roughly equivalent to the spectral width including the spectral line due to the NQR effect, as presented in Fig. 4. Even though, compared with results obtained under a steady field, the quality of the spectral lines is not high and the NQR effect is not very obvious, this was the first time that nuclear spin detection excited by a spin-echo pulse sequence was realized in a pulsed field and was of great significance for the development of PF-NMR.

In 2012, the HLD group built a complete spectrometer system suitable for high-field, high-frequency NMR experiments under pulsed fields. The upper-level computer program was written in LabVIEW, and the lower-level program was embedded in the NI system.[40] As shown in Fig. 5, the bandwidth range of the spectrometer could theoretically reach 500 kHz–2.7 GHz. Based on this spectrometer, a spin-echo pulse sequence was used to solve the dephasing problem in an inhomogeneous magnetic field. The transverse relaxation time T_2 of the nuclear spin system under a

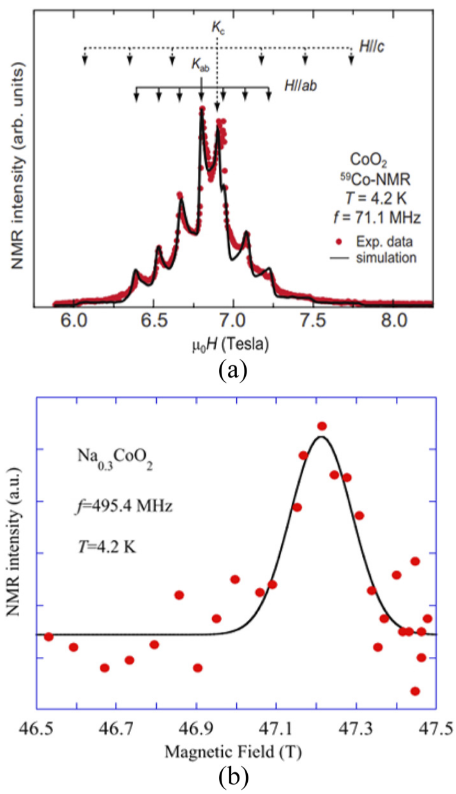

FIG. 4. (a) ^{59}Co NMR spectra under a steady field. Reprinted with permission from Kawasaki *et al.*, Phys. Rev. B **79**, 220514 (2009). Copyright 2009 American Physical Society. (b) ^{59}Co NMR spectra under a pulsed field. Reprinted with permission from Zheng *et al.*, J. Phys. Soc. Jpn. **78**, 095001 (2009). Copyright 2009 The Physical Society of Japan.

pulsed field was obtained for the first time, indicating that it is feasible to observe dynamic relaxation processes of NMR in ultrahigh pulsed fields. It has been speculated that the spin coherence time is long enough to allow further NMR experiments such as crystal structure analysis and electronic state capture.

In 2011, the group at the Laboratoire National des Champs Magnétiques Intenses (LNCMI) used a spin-coherent NMR spectrometer similar to that described in Refs. 38 and 41 to realize solid state measurements in PF-NMR experiments, observing ^{1}H and ^{93}Nb spectral lines at 30.4 T.[42] Two years later, this research group presented the detailed structure of the PF-NMR spectrometer, as shown in Fig. 6. The main difference from the HLD group's spectrometer is that a dual-channel Marconi 2024 RF signal generator was used, and a Lake Shore Model 340 temperature control system was configured at the sample end. Using this system, 48.8 T NMR experiments on YBCO were carried out, and the main and satellite peaks of ^{63}Cu and ^{65}Cu were observed.[43] This was the first time that NMR studies were performed on high-temperature superconductors in a pulsed high magnetic field.

As far as magnet development is concerned, the HLD group completed the design, construction, and testing of a PF-NMR experimental magnet. On the basis of 70 T/100 ms, they planned to build a 60 T/1000 ms long pulsed magnet.[44] With this goal, in 2012, they successfully built a 60 T/1500 ms long pulse magnet that stayed for about 70 ms at the maximum field level ($B_{max} \pm 1$ T).[45] The magnet structure is composed of a modular high-power capacitor bank and special copper alloy wire mixed with Zylon–Stycast composite reinforcement, which allowed NMR experiments to be performed at 52.2 T with a long pulsed flat top.

In 2016, the LNCMI group analyzed the spatial homogeneity of the magnetic field in a PF-NMR experiment.[46] It is generally accepted that the main reason for decreased homogeneity of high-field pulses is deformation of the magnet geometry rather than noise. By changing the winding direction of the local magnet coil and reducing the sample volume and center hole diameter of the magnet, the LNCMI study achieved a high degree of homogeneity of 10 ppm at 12 T over a sample volume of 2 mm^3–3 mm^3 in the central part of the magnet. Although this does not represent much of an advantage over superconducting magnets, the same method was used to achieve a spatial homogeneity of 33 ppm at 47 T, which improved the spatial distribution of magnetic flux at the level of pulsed high magnetic field intensity, as shown in Fig. 7. This further widens the scope for further development of NMR technology in pulsed field environments.

In terms of signal processing strategy, in addition to common problems such as radio-frequency interference (RFI) noise,[47,48] the

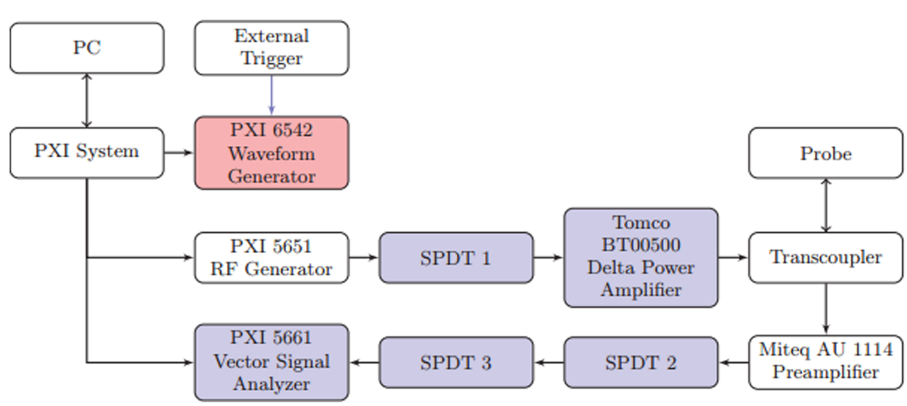

FIG. 5. Scheme of the pulsed NMR spectrometer at HLD. Reprinted with permission from Meier *et al.*, Rev. Sci. Instrum. **83**, 083113 (2012). Copyright 2012 AIP Publishing LLC.

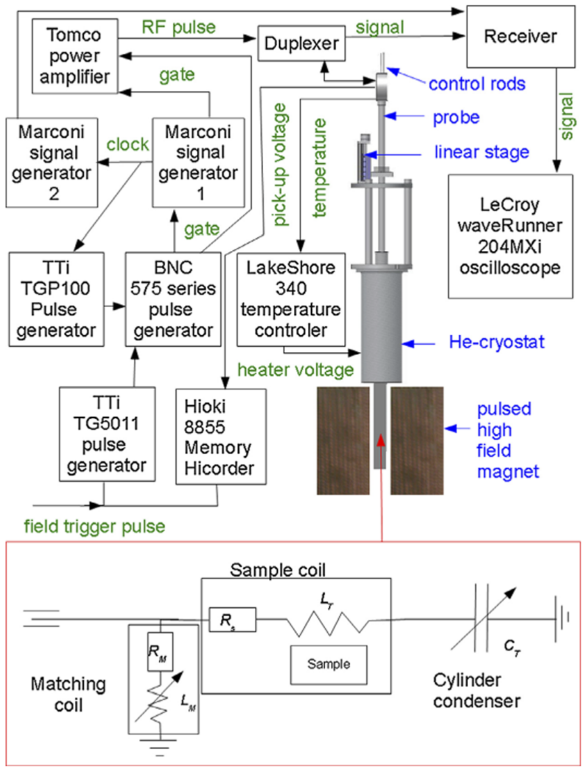

FIG. 6. Scheme of the pulsed NMR spectrometer at LNCMI. Reprinted with permission from Stork *et al.*, J. Magn. Reson. **234**, 30 (2013). Copyright 2013 Elsevier.

most important issue in PF-NMR is phase correction of FID signals modulated by the rapidly changing pulsed field. In 2007, the NIMS group published Ref. 49 on how to use deconvolution to calculate the NMR signal in a time-dependent field to achieve high resolution. In this method, the pick-up coil is used to monitor the real-time magnetic field strength, and the magnetic field fluctuations are divided into two parts: recognizable and unrecognizable. The unrecognizable part mainly refers to the initial offset or slow fluctuations with a period longer than a few milliseconds. Such fluctuations cannot be detected by the pick-up coil in an instantaneous measurement. The constant value is determined by adjusting all the FID spectral peaks collected in one discharge to the average position. Figure 8(a) shows the fluctuating curve obtained from a synthesis of five tests. After the initial fluctuations have been corrected, the induced voltage of the pick-up coil is double-integrated to obtain the phase offset, thereby realizing an interlock of magnetic field and phase. In this way, the FID signal correction process of a MAS-NMR experiment can be completed under the high field provided by a 30 T hybrid magnet. Two years later, the NIMS group further proposed a reference signal deconvolution compensation method for phase reconstruction in response to the large magnetic field fluctuations that occur in NMR experiments on liquid samples. The NMR signals of ^{1}H and ^{2}D were measured synchronously in the fluctuating field, and ^{1}H phase compensation was performed with the ^{2}D picked signal as a reference with high resolution.[50]

The LNCMI group used a similar method for obtaining the induced voltage in the additional pickup coil to estimate the phase offset. They performed deconvolution correction on the measured signal according to the feedback voltage value, and obtained an FID

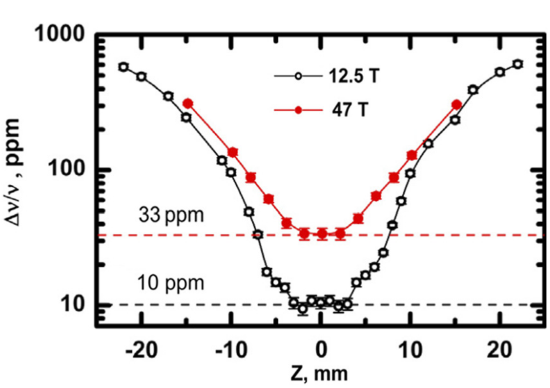

FIG. 7. Magnetic field homogeneity of the pulsed magnet at LNCMI at 12.5 T and 47 T. Reprinted with permission from Orlova *et al.*, J. Magn. Reson. **268**, 82 (2016). Copyright 2016 Elsevier.

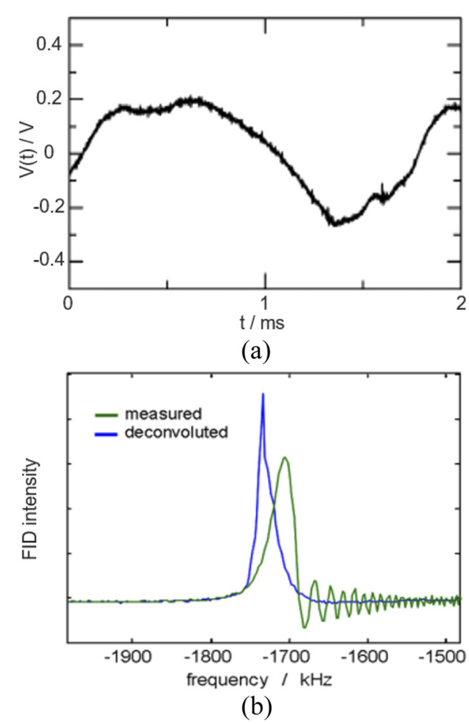

FIG. 8. (a) Initial value of the induced electromotive force measured synchronously with the FID signal. Reprinted with permission from Iijima *et al.*, J. Magn. Reson. **184**, 258 (2007). Copyright 2007 Elsevier. (b) ^{1}H spectrum before and after deconvolution. Reprinted with permission from Stork *et al.*, J. Magn. Reson. **234**, 30 (2013). Copyright 2013 Elsevier.

spectral line consistent with the steady field.[43] The result is shown in Fig. 8(b).

In 2011, the HLD group published a signal averaging algorithm for NMR experimental data in a pulsed field.[51] By fitting FID signals, the time-dependent $B(t)$ of the magnetic field was obtained, and the initial phase was then inverted by $B(t)$. The phase change of the FID signal was interlocked with the change in the magnetic field through the resonance gyromagnetic ratio to give the spectral analysis results for the FID signal. This method enables the correlation experiment to carry out signal averaging in a pulsed field similar to the way in which this is done in a steady state, which goes a long way toward solving the problems of rapid signal change and poor repeatability of the pulsed field. The resonance spectrum of 25/10 FID signals in 25/5 ms under a 7.7 T–7.8 T/61.7 T–62.2 T pulsed field was obtained, as shown in Fig. 9. This means that Knight/chemical shifts in a pulsed magnetic field can be measured, which allows nuclear magnetic electronic states to be studied and spin magnetization information to be obtained in high-field systems in a variety of applications, including biological, chemical, and condensed matter physics. This is an important achievement in the development of PF-NMR.

It is noteworthy that the above problems, such as phase correction and signal averaging, are all accomplished by $B(T)$ deconvolution, because they are only applied in a single-pulse scenario. However, in actual experiments, in order to extend high-field detection results to newly discovered field-induced systems, it is still necessary to measure the signal average value under multiple pulses. At the same time, judging from the current development of magnet technology, no matter which facility produces a pulsed high magnetic field, repeatability is limited, and the discharge mode means that it is impossible to achieve an accurate setting value for each peak magnetic field, and therefore the waveform in a certain region at the top cannot be completely reproduced. From this point of view, in 2016, the HLD team further proposed a method to demodulate the magnetic field intensity with the phase of the strong nuclear spin signal as the reference value, and they used the magnetic field strength to modulate the weak nuclear spin signal in turn. The NMR shifts of ^{27}Al and Linde A zeolite were detected under a maximum magnetic field of 58 T,[52] as shown in Fig. 10(a), thereby setting a precedent for high-field NMR multinuclear detection.

In addition, the longitudinal relaxation time T_1 is a very important measurement objective in conventional NMR experiments. However, it is very difficult to measure T_1 in a pulsed field, because it ranges between milliseconds and seconds, and the peak plateau time of the pulsed magnetic field is shorter than this. The HLD team presented a method for measuring T_1 in a fast relaxation system by using adiabatic inversion in the pulsed field. The measurement process is shown in Fig. 10(b). The T_1 values of 29 T/302 K aluminum powder and 58 T/308 K liquid gallium were successfully measured, with errors that were within the allowable fluctuation range.

In the same year, the HLD team further considered nuclear quadrupole energy other than Zeeman energy,[53] and introduced B_{max} as a normalization factor in the deconvolution average method in the signal processing. This method was applied to the spin dimer system $SrCu_2(BO_3)_2$ to observe the NMR phenomenon of the ^{11}B system at 54 T. An overview of the procedure is shown in Fig. 11. The result shows that the problem of spectral line broadening caused by inhomogeneity, instability, and poor repeatability of the magnetic field has largely been solved. Compared with the previous single-pulse phase correction, a more feasible high-field NMR signal processing method under multi-pulse experiments has been proposed, which improves the quality of the spectrum and gives hyperfine interaction information at the microscopic electronic state level that cannot be obtained under low-field conditions. This provides a demonstration of the analysis of nuclear spin NMR spectra in a pulsed high magnetic field.

In general, many effective signal processing methods are available that allow higher-quality FID spectral lines to be obtained in NMR detection under unsteady magnetic fields. The methods described in this paper are listed in Table I.

Up to now, PF-NMR technology has achieved the four most important objectives of observation in experiments: the Knight/chemical shift, the NQR effect, the longitudinal relaxation time T_1, and the transverse relaxation time T_2.

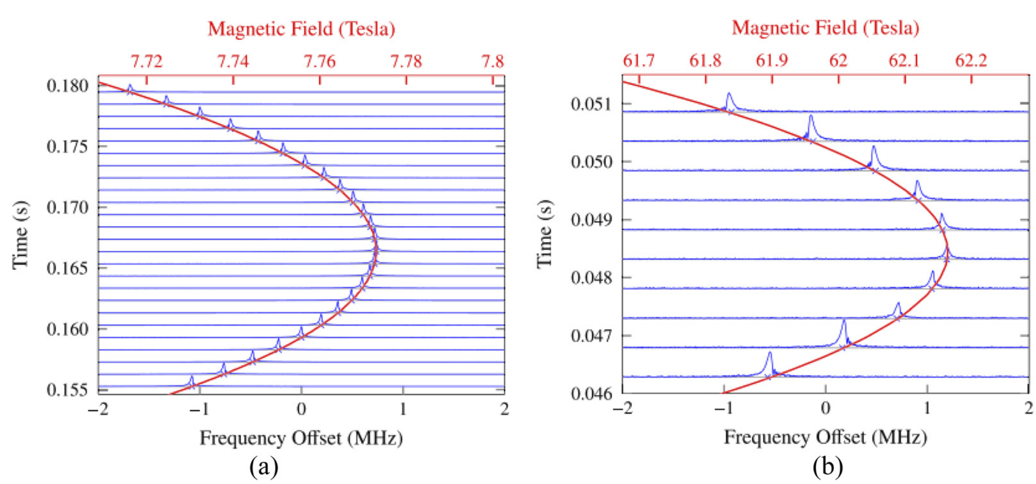

FIG. 9. Spectrogram of the FID signal of a single-pulse peak segment: (a) 7 T; (b) 62 T. Reprinted with permission from Meier *et al.*, J. Magn. Reson. **210**, 1 (2011). Copyright 2011 Elsevier.

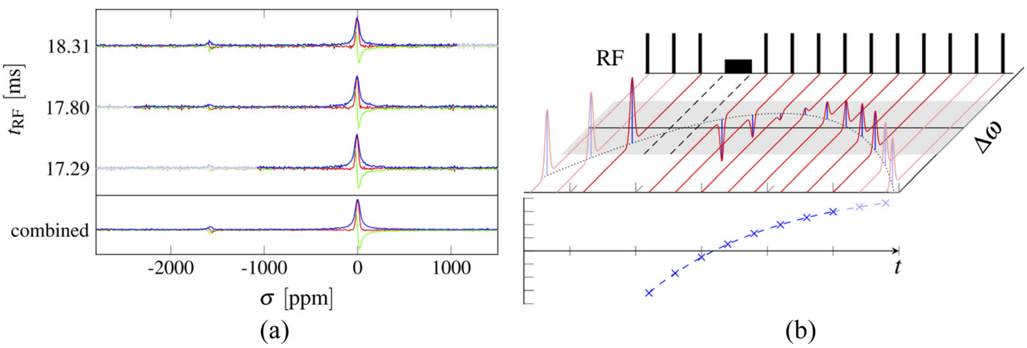

FIG. 10. (a) FID signals of Linde A (weak, left) and ^{27}Al (strong, right) under a 55.7 T pulsed field. (b) Adiabatic reversal experiment for measuring T_1 in a pulsed field. Reprinted with permission from Kohlrautz *et al.*, J. Magn. Reson. **263**, 1 (2016). Copyright 2016 Elsevier.

With the development of high-field NMR over the last 20 years (Table II), it has been demonstrated that NMR experiments are quite feasible in pulsed magnetic fields. Research teams from Germany, France, and Japan have cooperated with the high-magnetic-field laboratories and have made outstanding achievements in related research. Although there have not been many papers published in this area to date, and the quality of NMR spectral analysis in pulsed magnetic fields remains far lower than that in steady fields, the huge development potential of PF-NMR provides a great incentive for high-magnetic-field research centers worldwide to focus more on this area and gradually move from exploration to application.

From an interdisciplinary point of view, high-magnetic-field technology and NMR have a strong correlation. If a high-field and high-frequency NMR technology using flat-top pulsed magnetic fields (FTPMFs) can be developed on existing experimental platforms, and background fields with stability and homogeneity comparable to those of a steady-state magnetic field can be realized, it should be possible to use PF-NMR in a wider range of applications in biology, medicine, and solid state physics. This will not only promote the development of pulsed high-magnetic-field technology, but will also have long-term significance for innovation in NMR detection methods.

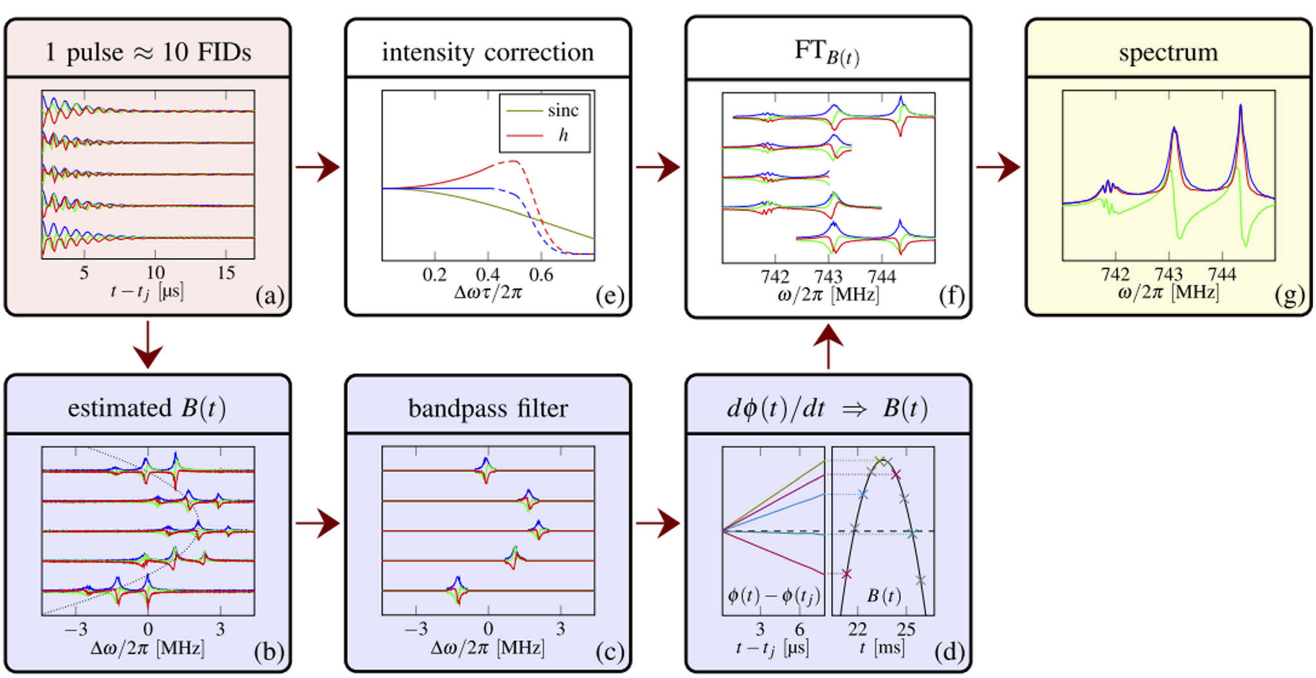

FIG. 11. Overview of procedure for reconstruction of broad spectra in a pulsed magnetic field using the normalized deconvolution method. For more details, see Ref. 53. Reprinted with permission from Kohlrautz *et al.*, J. Magn. Reson. **271**, 52 (2016). Copyright 2016 Elsevier.

TABLE I. NMR signal processing strategies in unstable magnetic fields.

Facility	Reference	Magnet[a]	Acquisition of $B(t)$	Phase correction
NIMS	49	Hybrid	Pick-up coil	Deconvolution averaged
HLD	51	Resistive	L-M algorithm	Deconvolution averaged
HLD	53	Resistive	Phase demodulation	Normalized deconvolution
LNCMI	43	Resistive	Pick-up coil	Deconvolution

[a]The devices that generate unstable high magnetic fields are generally divided into hybrid magnets and resistive magnets. The former produce magnetic field profiles closer to those of permanent magnets or superconducting magnets with a lower intensity, while the latter produce pulsed magnetic fields with greater fluctuation but higher intensity.

III. RESEARCH PROSPECTS

There have been a number of proposals for practical applications of PF-NMR, with the ability to carry out NMR experiments under higher magnetic fields offering new research opportunities in many areas.

A. Bio-macromolecular dynamics

As one of the main methods for structural analysis of biological macromolecules, NMR has been widely used to reveal the relationship between structure and function of proteins and nucleic acids. Compared with other detection methods, NMR can capture the instantaneous dynamic structure of biological macromolecules, with the molecular characterization being closer to that in physiological states, and it can provide a better reflection of the relationships between structure, dynamics, and function. For example, although interactions between proteins are weak, they are fundamental to cell signal transduction and many other important cellular processes. Taking advantage of the nuclear Overhauser effect (NOE) between molecules, it is possible to use NMR spectroscopy to detect ultraweak interactions between proteins and determine their skeletal structure[54]

Recent years have seen the successful capture of the protein complex with the currently known weakest interaction strength (dissociation constant K_d up to 25 mM) using paramagnetic NMR technique, together with a structural analysis at atomic resolution, as can be seen in Fig. 12.[55] A new type of rigid paramagnetic probe with unpaired electrons was developed to label the protein, and the subtle changes in protein structure were then successfully observed by NMR, with a detection spatial resolution reaching 1 Å.[56] Moreover, protein site-specific labeling based on unnatural amino acids and a label-free NMR method has also been promoted, greatly expanding the scope of application of magnetic resonance techniques.[57–59]

The SNR is the key parameter determining NMR detection sensitivity. Because the interval between nuclear spin energy levels is very small (the smallest among almost all types of absorption spectra), the energies and sensitivity of NMR are very low (e.g., smaller than those in electron spin resonance[60,61] by a factor of 1000 or more). In recent years, methods such as dynamic nuclear polarization (DNP) have been proposed to excite electron nuclear double resonance with the aim of solving this problem, but it is difficult and expensive to manufacture high-power millimeter-wave microwave sources. Therefore, the most direct way is still to improve the SNR based on existing NMR experiments. One method is to increase the number of particles distributed in an energy level by increasing the concentration of the sample. However, the sample concentration is usually limited by natural abundance and extraction and separation techniques. Another convenient approach is to increase the magnetic field intensity to widen the energy level interval, thereby obtaining a greater energy level difference and a higher Larmor frequency of atomic

TABLE II. Research status of NMR in unsteady high magnetic fields worldwide.

Facility	Year	Reference	B_{max} (T)	Resonance frequency (MHz)	Temperature (K)	R_{probe} (mm)	RF sequence	Target nucleus (object)
HLD	2003	31	12	140	300	3	$\frac{\pi}{2}$ (0.5 μs)	^{63}Cu (shift)
	2003	31	33	360	300	2	$\frac{\pi}{2}$ (0.5 μs)	^{63}Cu (shift)
	2004	33	58	375	300	3	$\frac{\pi}{2}$ (0.5 μs)	^{2}D (shift)
	2005	37	56	2400	300	6	$<\frac{\pi}{2}$ (0.3 μs)	^{1}H (shift)
	2012	40	62	400	...	6	$\frac{\pi}{2}(1\ \mu s)-\tau(150\ \mu s)-\pi(2\ \mu s)$	^{2}D (T_2)
	2016	52	58	600	308	16	$\ll\frac{\pi}{2}$	^{69}Ga (shift, T_1)
	2016	53	54	740	2	...	$\frac{\pi}{2}$ (0.2 μs)	^{11}B (shift, NQR)
Okayama university	2010	41	48	495	...	...	$\frac{\pi}{2}(2.5\ \mu s)-\tau(20\ \mu s)-\pi(5\ \mu s)$	^{59}Co (shift, NQR)
LNCMI	2011	42	30	300	80	...	$\frac{\pi}{2}(4.7\ \mu s)-\tau(20\ \mu s)-\pi(9.4\ \mu s)$	^{93}Nb (shift)
	2013	43	47	300	2.5	...	$\frac{\pi}{2}(0.8\ \mu s)-\tau(3.9\ \mu s)-\pi(1.6\ \mu s)$	^{63}Cu/^{65}Cu (shift, NQR)

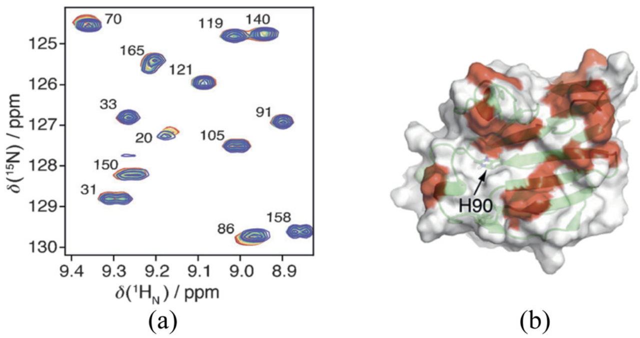

FIG. 12. (a) EIIA^{Glc} titration results with an 800 MHz NMR spectrometer. (b) Surface mapped by residues with chemical shift perturbations >3 Hz. Reprinted with permission from Xing *et al.*, Angew. Chem., Int. Ed. **53**, 1 (2014). Copyright 2014 John Wiley and Sons.

magnetic moment precession. This enhances the useful signal in the NMR experiment and significantly improves the SNR.

At present, the maximum available pulsed field intensity has reached 80 T–100 T, generated at high-magnetic-field research institutions, the maximum flat-top magnetic field has reached 64 T, and the platform period has reached tens of milliseconds or even longer. Collecting nuclear magnetic data under ultrahigh magnetic fields can greatly shorten the experimental time and significantly improve the acquisition efficiency of massive multidimensional NMR data. In addition, the structural changes of certain biological macromolecules with specific biological functions are dynamic. A single sample can be detected with different magnetic field strengths under a pulsed magnetic field, and dynamic information about the protein structure can then be inferred from the magnetic resonance characteristics (relaxation, chemical shift, chemical exchange, etc.). A large amount of NMR information can be obtained through rapid sampling under different magnetic field intensities, which is helpful for analyzing the dynamic characteristics of protein structures in the process of their function. Clearly, PF-NMR can provide a high-precision and high-resolution method for analyzing structural information on biological macromolecules, thereby helping to solve a number of important basic biological problems.

B. Condensed matter physics

In condensed matter physics, NMR is often used to study the interaction between nuclear systems and a magnetic field, the interaction between nuclei and the outside environment, and the relaxation of nuclear systems. Owing to the hyperfine interaction between the electronic and nuclear moments, the electronic system can be directly detected through the nucleus, thereby providing valuable information on many different phenomena,[7] with the advantages of high spatial resolution and flexible element selection. NMR experiments can be used to observe the characteristics of some unconventional materials, including physical properties such as the Knight shift, NQR, and relaxation time, in order to detect spin density waves (SDWs), electron nematic order, superconducting energy gap changes, etc. The extreme conditions generated by a pulsed field may produce some field-induced effects that cannot be observed in low fields, and PF-NMR is a powerful tool for detecting these abnormal phenomena.

1. Unconventional superconductors

It has been found that field-induced effects are very common in unconventional superconductors. For example, in a high field, the inner and outer regions of the unconventional superconductor vortex core with nodes in the gap can be clearly distinguished, and spin diffusion and vortex vibrations can be suppressed, making observations much easier and more conclusive than in low fields.[62] Further studies have proved that a high magnetic field can not only suppress the superconducting state,[63] but also induce some exotic superconducting states.[64,65] Both conventional and unconventional superconductors have unique nuclear spin magnetization and energy gap properties,[66,67] which can be detected by NMR, and the crystal structure of topological superconductors can also be studied using the Knight shift.[68]

Despite the growing interest in the study of superconductivity in pulsed high magnetic fields, there has been a lack of detection techniques that are suitable for use with such pulsed fields. For example, in a low-dimensional unconventional superconductor, when the upper critical magnetic field H_p determined by the Pauli splitting effect is higher than the upper critical magnetic field generated by the orbital effect, an unconventional phase state of Cooper pairs with nonzero total momentum and a spatially nonuniform order parameter can be induced by fields higher than H_p. This leads to the appearance of a normally conducting region in the superconductor,[69–71] which is called the Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) phase. This phase was originally discovered when a sufficiently strong magnetic field parallel to the conducting plane was applied to a quasi-two-dimensional superconductor. Under this strong in-plane magnetic field, as a result of the Zeeman effect, the Fermi surface will be split. Furthermore, some electrons are polarized, and so the Cooper pair whose central momentum is zero is destroyed in this case, and a new type of pairing state becomes stable. The Cooper pair with finite nonzero momentum will bring about spontaneous spatial symmetry breaking and periodic modulation. Although some NMR experiments have provided good evidence for the FFLO state in organic superconductors,[72–74] the existence of this state is still controversial, and there is an urgent need for more phase transition information from ultrahigh-magnetic-field experiments. Heat capacity and PF-NMR experiments with a magnetic field strength greater than H_p should be able to facilitate observation of the FFLO phase in unconventional superconductors.

It is evident that PF-NMR has better performance than NMR with steady-state fields in some respects. The LNCMI team carried out 48.8 T PF-NMR experiments on YBCO, the second class of high-temperature superconductors, and observed the spectral lines of ^{63}Cu and ^{65}Cu,[43] comparing these with their previous NMR results for Cu under a steady magnetic field.[23] Under the high field, the observed gyromagnetic ratio and satellite line position were consistent with those under the low field, and a more obvious spectral splitting (at 554 MHz) could be obtained, as shown in Fig. 13. Although the SNR was not ideal, it was still clear that the PF-NMR technique was superior to steady-field NMR for observing atomic hyperfine interactions. More importantly, the application of NMR with a pulsed high magnetic field will make it possible to study the unconventional

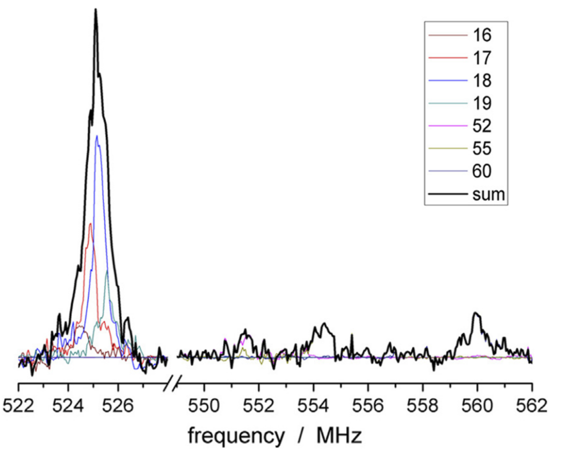

FIG. 13. Resonance spectra of $YBa_2Cu_3O_x$ in a pulsed 47 T field. The black solid line is the sum of several experiments (2.5 K). Reprinted with permission from Stork *et al.*, J. Magn. Reson. **234**, 30 (2013). Copyright 2013 Elsevier.

conducting state of high-temperature superconducting samples at temperatures and doping regimes where NMR experiments could not previously be performed.

2. Magnetic materials

In recent years, there have been extensive studies of phase transition mechanisms in quantum magnetic systems, ranging from quantum spin liquids with topological order[75] to deconfined quantum critical points disallowed by Landau–Ginzburg–Wilson symmetry-breaking theory,[76] first-order phase transition with continuous symmetry,[77] and Bose–Einstein condensation.[78] With the emergence of these new phenomena, NMR has become an important tool to study the magnetic structure of the associated systems. Take ferromagnetic and antiferromagnetic phase transitions as examples. If a ferromagnetic phase transition occurs in a system, since the total magnetic field to which each nuclear spin is exposed is the sum of the external magnetic field and the nucleus's own internal field, then a large NMR shift will be generated; if a antiferromagnetic phase transition occurs in the system, then the total magnetic field on half of the atoms is the sum of the external and internal fields, while that on the other half of the atoms is the difference between the external and internal fields, and consequently the spectral peaks will split. On the basis of these characteristics, it is possible to infer the magnetic structure of a material based on NMR spectral information. Furthermore, in higher-field NMR experiments, some magnetic materials can exhibit different phase states from those in a low field, which provides a new perspective for related research.

For example, in a 2009 NHMFL publication, it was shown that the heavy fermion antiferromagnetic material $CeIn_3$ had an abnormal skin depth at 45 T.[79] Ten years later, the LNCMI team conducted PF-NMR experiments on $CeIn_3$ again. Within the acceptable range of resolution, the obvious changes in the NMR spectrum at different temperatures confirmed the existence of a magnetic phase transition from the paramagnetic state to the antiferromagnetic state. However, Fig. 14 shows that at the same temperature, there is almost no change in the NMR spectral peak under three different magnetic field intensities: a steady 10.7 T field, a 36.4 T hybrid magnetic field, and a 52 T pulsed high magnetic field.[80] This indicates that the abnormal phenomenon exhibited by ^{115}In at 45 T cannot be attributed simply to the change in magnetic structure or to distortion of the crystal structure and the charge density distribution, but rather it is possible that hyperfine coupling changes the properties of the ^{115}In electric field gradient.

An investigation of the well-known frustrated magnetic material $SrCu_2(BO_3)_2$ again illustrates the unique advantages of PF-NMR. As a quasi-two-dimensional spin system, $SrCu_2(BO_3)_2$ is the prototype of a material with a highly symmetric and frustrated Shastry–Sutherland Hamiltonian. Its average magnetization shows a strong background field dependence, as shown in Fig. 15(a).[81–84] In 2016, the HLD team studied its NMR behavior in a pulsed magnetic field. A conventional quadrupole spectrum was found at 54 T/119 K,[53] but when the temperature dropped to 2 K, further splitting peaks [blue curve in Fig. 15(b)] were observed, which was similar to the behavior of the material in a 41 T steady magnetic field [black curve in Fig. 15(b)]. This result is consistent with the magnetic superlattice in Fig. 15(c), namely, the spin superstructure for the plateau phase shows the triplet dimers mentioned in Ref. 81. Compared with the NMR experiment under a 41 T steady field, the use of the 54 T pulsed field significantly

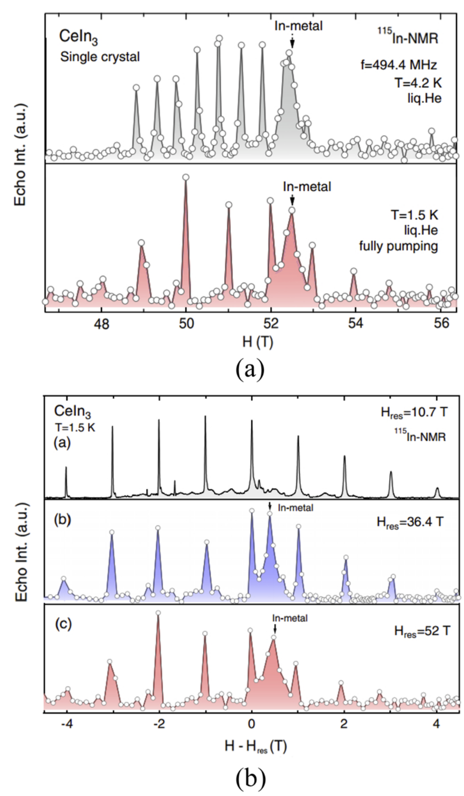

FIG. 14. (a) $CeIn_3$ NMR spectra (56 T) at different temperatures. (b) $CeIn_3$ NMR spectra (1.5 K) at different magnetic field intensities. Reprinted with permission from Tokunaga *et al.*, Phys. Rev. B **99**, 085142 (2019). Copyright 2019 American Physical Society.

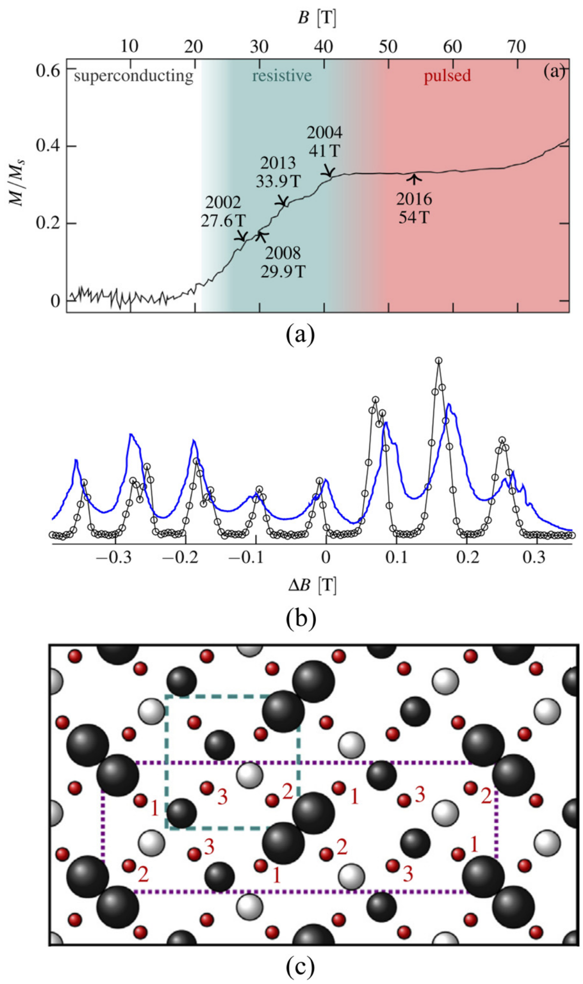

FIG. 15. (a) Curve of average magnetization of $SrCu_2(BO_3)_2$ vs magnetic intensity.[81–84] (b) NMR spectra of ^{11}B under pulsed 54 T (blue) and steady 41 T (black) magnetic fields (2 K). (c) Magnetic superlattice in the 1/3 magnetization plateau. Reprinted with permission from Kohlrautz *et al.*, J. Magn. Reson. **271**, 52 (2016). Copyright 2016 Elsevier.

reduces the experimental energy consumption, improves the experimental efficiency, and broadens the available magnetic field range. With regard to the 2/5 and 1/2 magnetization plateaus mentioned in Refs. 85 and 86, further research under higher pulsed magnetic fields (e.g., >75 T) is warranted.

3. Nematic materials

Nematicity here refers to a liquid crystal phase in an electronic state that is similar to the nematic state in liquid crystals. The preferred orientation formed by nematic electrons destroys the rotational symmetry of the crystal, exhibiting short-range order and long-range disorder. In an NMR experiment, the spin fluctuation state is inferred from the observed Knight shift and the temperature dependence of $1/(T_1 T)$. When the background field intensity is high, a field-induced nematic phase transition may appear in some strongly correlated systems, which is of great significance for both theoretical and experimental research.

Take $LiCuVO_4$ as an example. Kazuhiro Nawa's research group at Kyoto University has studied the NMR behavior of ^7Li and ^{51}V in 4 T–10 T steady magnetic fields. They observed that the energy gap of ^{51}V above 10 T was suppressed, reflecting a phase transition from a spiral spin form to a spin density wave (SDW) state at low field.[87] They further studied the change in the energy gap of ^{51}V at a 45 T steady field provided by a hybrid magnet and pointed out that ^{51}V may continue to change from the SDW state to a spin nematic phase in the magnetic field range 40.5 T–41.4 T ($\mathbf{H} \parallel \mathbf{c}$).[88] The LNCMI group used a pulsed high-magnetic-field technique to further increase the background field intensity and obtained a PF-NMR spectrum of $LiCuVO_4$ at 56 T, as shown in Fig. 16.[89] The result shows that the phase transition from a SDW state to a magnetic saturation state occurs in the range 42.41 T–43.55 T with increasing magnetic field intensity ($\mathbf{H} \parallel \mathbf{c}$). In this magnetic field range, the normalized spin polarization S_z/S_z^{sat} is linear, while the internal magnetic field ΔH_{int} remains constant. The system exhibits an obvious spin nematic phase. This experimental result is slightly different from the nematic appearance range obtained by Nawa's group, which may be caused by different defect concentrations in the sample.

In recent research,[90] Yoshimitsu Kohama's team at the University of Tokyo has studied the spin phase sequence of $LiCuVO_4$ by NMR. In experiments below 27.5 T, with a steady magnetic field, the fitted nematic phase NMR line shape was found to be close to the saturated state, while in experiments above 28 T, with a 33 T pulsed magnetic field, the specific heat and magnetocaloric effect (MCE) were measured. The magnetic order detected in this study once again provided evidence for a nematic phase state of spin 1/2 in the magnetic frustration lattice from a thermodynamic point of view, further illustrating the reliability of results obtained by means of PF-NMR.[89]

In contrast to normal materials, nematic materials do not have the rotational symmetry of crystals and retain time reversal symmetry, which is different from the traditional magnetic sequence. However, in the case of $LiCuVO_4$, this exotic phenomenon cannot be observed in the lower magnetic fields provided by ordinary superconducting magnets or permanent magnets, while the use of hybrid

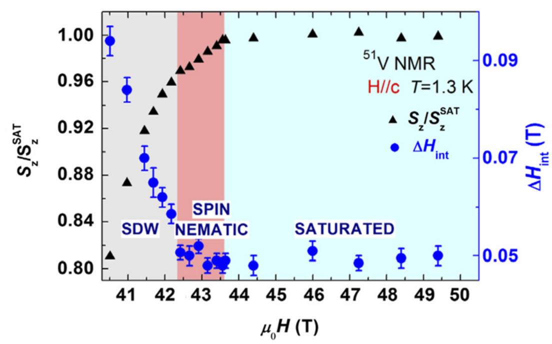

FIG. 16. Field dependence of the normalized spin polarization S_z/S_z^{sat} and distribution widths of the internal magnetic field ΔH_{int} obtained from the ^{51}V PF-NMR spectra in $LiCuVO_4$ ($\mathbf{H} \parallel \mathbf{c}$). Reprinted with permission from Orlova *et al.*, Phys. Rev. Lett. **118**, 247201 (2017). Copyright 2017 American Physical Society.

magnets is restricted by the power supply and cryogenic system. However, by using PF-NMR methods, it is easy to obtain excellent results for such materials.

IV. BOTTLENECK PROBLEMS

At present, the development of nuclear magnetic resonance technology is focused mainly on magnets, spectrometers, and probes. However, to facilitate the further development of PF-NMR in particular, it is also necessary to consider three particular issues.

A. Flat-top pulsed magnetic fields

High magnetic fields used in NMR can be divided into two types according to their duration: steady fields and pulsed fields. The intensity of a steady field is constant and persistent, while that of a pulsed field changes greatly and lasts for a short time.[91,92] The three main types of steady strong magnetic field are those generated by permanent, superconducting, and hybrid magnets, respectively, while pulsed high magnetic fields are usually generated by resistive magnets.

Owing to their characteristics of high stability and long duration, steady high magnetic fields are widely used in NMR. Because of their zero resistance, superconducting materials have the apparent merits of low heat loss and uniform conduction current and are commonly used to generate steady magnetic fields. Therefore, commercial NMR spectrometers based on superconducting magnets are in widespread use in medicine,[93] the study of biological macromolecules,[54,94,95] solid state physics,[23,39,87,96] and other research on organic and inorganic materials.[97] Nevertheless, superconducting materials are limited by their critical magnetic field and critical current, and so the range of magnetic fields that can be reached is subject to severe constraints. As mentioned above, the continuous development of NMR techniques has provided an incentive for developing ways to achieve further increases in background field intensity. The requirements of some experimental investigations have already exceeded the design limits of available steady high-magnetic-field technology. At the same time, however, pulsed magnets can generate fields of more than 50 T, and thus provide a route to obtaining insight into material properties in the regime up to 100 T. This is manifestly the most direct way to meet the magnetic field intensity requirements for ultrahigh-field NMR research.

A stable and homogeneous magnetic field is a basic requirement for an NMR experiment. Most commercial solid state NMR equipment requires that the homogeneity of the steady magnetic field be better than 10 ppm over mm/DSV and that the stability be better than 10 ppm/h. For this reason, various shimming methods have been proposed, such as field-frequency locking, additional coil compensation, and installation of flux stabilizers.[108] However, these methods are limited by the aperture and pulse power of the pulse magnet, and so they cannot be simply copied for the PF-NMR technique. In the case of a pulsed magnetic field, the discharge method determines the inherent time dependence and spatial distribution of the magnetic field. The temporal stability and spatial uniformity of pulsed magnets are usually as high as several thousand ppm or even tens of thousands of ppm near the peak, and the Larmor resonance frequency is directly proportional to the magnetic field strength. Under these circumstances, any instability of the magnetic field will cause violent fluctuations of the resonance frequency, which is reflected in the spectrum of the FID signal, leading to inhomogeneous broadening of spectral peaks and, in severe cases, to aliasing. This will make the NMR displacement blurred, resulting in the measured relaxation time being much smaller than the actual value. Until recently, the range of materials that could be detected by PF-NMR was quite limited.[7] For systems with long relaxation times, the millisecond-level duration of the pulsed magnetic field is too short to cover a complete relaxation process, thus failing to meet the basic conditions for NMR detection. Even though the peak width of a robust spin correlation system measured in a high magnetic field is usually more than 10 kHz–100 kHz, which greatly tempers the demands on the homogeneity and stability of the background field, it is still necessary to control the resolution within a few hundreds of ppm to achieve acceptable resolution. Moreover, the repeatability of pulsed strong magnetic fields is poor, and their accuracy of restoration is not sufficient to accumulate signals from multiple experiments. In this case, the NMR detection method almost completely loses its advantages, and pulsed magnets were therefore long considered unsuitable for NMR.[109]

A flat-top pulsed magnetic field (FTPMF) refers to a kind of magnetic field that stabilizes the pulsed magnetic field at the crest within a certain period of time. It is able to form a profile similar to a steady magnetic field in the platform segment. Table III lists the current technical advances with respect to the use of FTPMFs in large facilities.[45,98–107] FTPMFs combine the advantages of the high stability of steady magnetic fields and the high field strengths of pulsed magnetic fields, and thus provide a new basis for NMR experiments that cannot be performed using steady magnetic fields with low field strength.

Since 2000, research institutions in Germany, Japan, France, and elsewhere have successively carried out NMR studies with pulsed high magnetic fields. ^{1}H, ^{63}Cu/^{59}Co, and ^{63}Cu/^{65}Cu NMR spectra have been observed at 56 T, 55 T, and 48.8 T respectively (Table II), and the highest RF frequency has reached 2.4 GHz. However, the use of pulsed magnetic fields in these experiments has encountered problems such as short flat-top duration and insufficient stability (existing PF-NMR experiments have stabilities not less than a few hundred ppm), resulting in failure to meet relaxation time conditions, broadening of FID signal linewidth, baseline distortion, and phase error. These cause difficulties in NMR spectral analysis, leading to poor signal quality. As mentioned above, HLD and LNCMI have published deconvolution algorithms to solve the problem of insufficient stability, and have thereby improved the resolution of FID spectral lines, but this is only part of signal post-processing, and does not improve the stability of the background magnetic field itself. It is worth noting that, in addition to stability, the homogeneity and repeated additivity of the background magnetic field are important concerns even for traditional NMR, but there have been few studies of these issues in the context of PF-NMR. All of these things show that the current state of PF-NMR technology is far from mature and further developments are needed.

A key task to allow high-field, high-frequency NMR experiments to be carried out is the development of an FTPMF system with high stability, homogeneity, and repeatability. This will involve, among other things, optimization of the magnet structure to improve spatial homogeneity at the sample position, the development of power supplies that can provide high-stability, ripple-free, and high-current excitation to generate strong magnetic fields with long flat-top duration, and satisfaction of requirements on relaxation time and NMR signal acquisition without loss of quantum controllability of the strong magnetic field.

TABLE III. Progress in FTPMF research worldwide.

Facility	References	Year	Power supply	B_{max} (T)	Duration (ms)	Stability (ppm)	Advantage	Limitation
UvA, NLD	98 and 99	1985	Grid rectifier	40	150	…	First appeared	Deleterious effects on the power gird
NHMFL, USA	100	1996	650 MJ generator	58.5	140	…	High B_{max} and long duration	High-power generator
TU Wien, AUT	101	2004	Grid rectifier	40	100	…	Long duration	Uncertain stability
HLD, GER	45	2012	50 MJ capacitor bank	55.2	70	18 000	High B_{max} and long duration	Heavy device (1200 kg) and long cooling time (8 h)
WHMFC, CHN	102	2012	185 MJ generator	50	100	5 000	Run smoothly	High power ripple
WHMFC, CHN	103	2014	900 × 200 Ah battery bank	25	200	300	High B_{max}	High PWM ripple
ISSP, JPN	104	2015	900 kJ capacitor bank	60.64	2	85	High stability	Short duration
WHMFC, CHN	105	2020	1400 × 200 Ah battery bank	23.37	100	65	High stability	Low B_{max}
WHMFC, CHN	106 and 107	2020	12 MJ capacitor bank	65	10	3 000	Low energy consumption	Open-loop control system

B. High-frequency spectrometer

The spectrometer is at the core of any NMR experiment. Figure 17 shows the overall structure of a current commercial spectrometer that is suitable for the working environment of a steady-state low-intensity magnetic field. In a pulsed high magnetic field, for example, when the magnetic field intensity is higher than 60 T, even a material with a low spin ratio will excite a resonance frequency of hundreds of megahertz, while for a material with high spin magnetic ratio, the resonance frequency may reach several gigahertz. In recent years, more powerful (and expensive) NMR spectrometers have appeared on the market. However, owing to limitations on the strength of the background field, the conventional frequency band is usually between 10 MHz and 400 MHz, so there is no need for NMR spectrometers with upper limits at the gigahertz level. By contrast, for NMR in pulsed high magnetic fields, there is an urgent requirement for NMR spectrometers suitable for a high-field and high-frequency environment.

First of all, to operate at high field strength when observing nuclei with a high spin ratio, the NMR spectrometer must support a resonance frequency much higher than the common resonance frequency in NMR experiments (e.g., the Larmor frequency of ^{1}H at 60 T will reach 2.6 GHz). Second, the temporal stability and spatial homogeneity of the pulsed magnetic field must be considered. On the one hand, because of the inherent time dependence of the magnetic field, the resonance frequency generated by each RF signal is unknown, so the NMR frequency will fluctuate continuously. On the other hand, because the experimental system is in the background of an ultrahigh magnetic field, these fluctuations will be amplified several times, and therefore the receiver needs a real-time bandwidth of at least tens of megahertz. Third, the phase of the collected FID signal is different, and direct averaging is not allowed, and so all data points must be stored in memory, waiting for subsequent correction processing. Therefore, compared with a steady-state NMR experiment, PF-NMR will generate a large amount of data in a short time, which imposes more stringent requirements on the storage capacity of the spectrometer. Besides, the ultrahigh magnetic field enlarges the Larmor frequency range, meaning in the RF power amplifier must maintain high power and small attenuation over a wide frequency range. These strict requirements on the power amplifier will significantly increase the investment cost of establishing an NMR spectrometer. Finally, since the holding time of a pulsed high magnetic field is very short, the sequence structure of the NMR spectrometer and the magnetic field generator must be set through a reasonable timing system to achieve precise digital control, so as to ensure the orderly calling of working modules such as the magnetic field trigger, RF trigger, and duplexer switching.

The construction of a PF-NMR spectrometer is a systematic project involving both software and hardware aspects. The hardware part includes a pulse sequence programming module, an RF excitation module, an amplifier module, an acquisition module, and an RF analysis module. The software part includes timing control and data analysis programs. The design goal is to have a broadband low-noise RF circuit, a fast receiver recovery time, accurate pulse programming, continuous data acquisition, and automatic data analysis functions, such that the high-field NMR spectrometer system will be universal and easy to replicate. This will allow a variety of researchers to conduct series of NMR studies under extremely high magnetic fields.

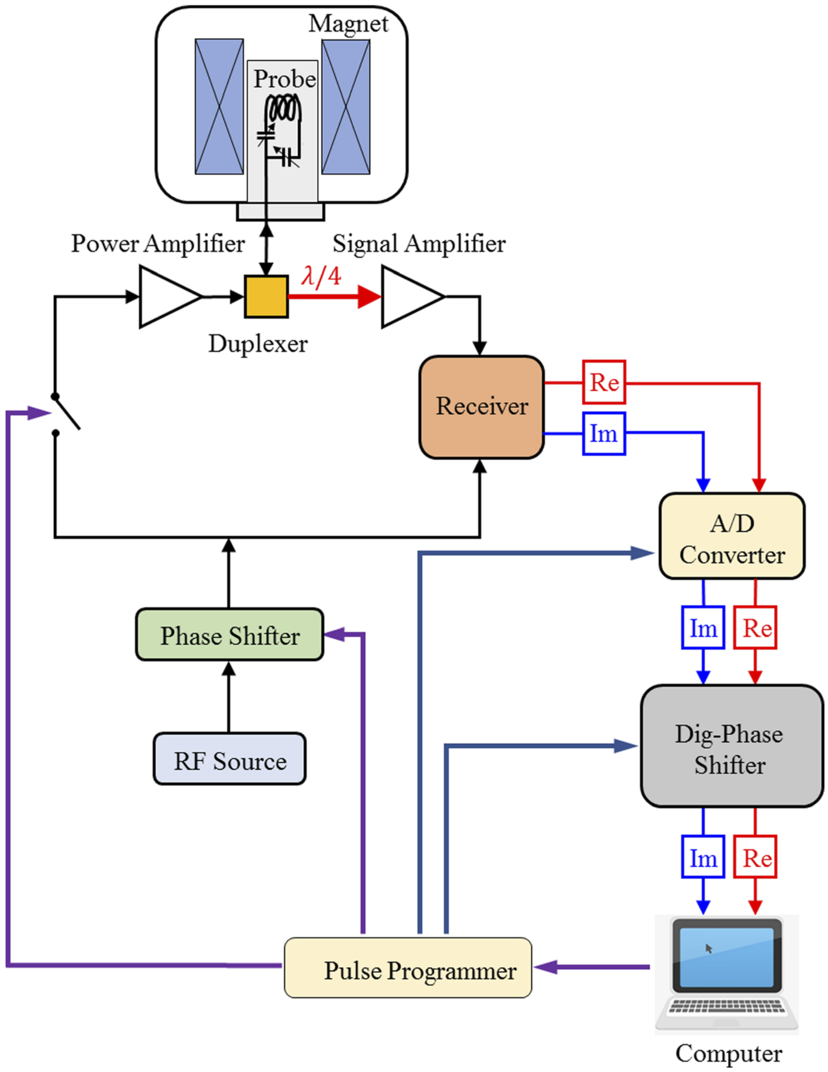

FIG. 17. Structure of a traditional NMR spectrometer.

C. Probe

In any NMR experiment, the probe carrying the sample is a key part. With the increasing application of NMR to investigate materials in extreme environments such as high pressures and strong magnetic fields,[110] there is a need to develop probes with a wide tuning range, accurate matching performance, good robustness, controllable strain, and coverage of the entire frequency range required by the nuclear resonance in the corresponding magnetic field.[7,111] Such probes should be able to provide samples with reliable signal transmission conditions and a stable loading environment. The space available for scientific experiments is usually located only at the center of the magnet aperture,[112] as shown in Fig. 18. Therefore, the diameter of the NMR probe for pulsed field is limited to a very small range. Taking a FTPMF of 60 T/2 ms/30 ppm as an example, the diameter of the aperture channel through which the probe can enter and exit is only 12 mm,[104] which is much smaller than the typical diameter of the probes used in ordinary steady magnetic fields.

Apart from the aperture limitations, a PF-NMR probe will also be affected by factors such as sample positioning, an inhomogeneous magnetic field distribution, electromagnetic noise, structural stresses, and temperature variations. Since the distribution of a pulsed high magnetic field is not as controllable as that of a steady field, it is difficult to accurately position the sample in the aperture, and the rapidly changing magnetic field may cause eddy currents in the *LC* coil of the probe, which generate a locally asymmetric magnetic field. This leads to distortion of the magnetic field in the aperture, thereby increasing the uneven broadening of the resonance signal. Worse still, strong electromagnetic noise and structural stress will be excited at the moment of discharge, which imposes stringent requirements with regard to electromagnetic shielding and structural stability of the probe. Finally, given that the pulsed magnetic field is usually immersed in liquid

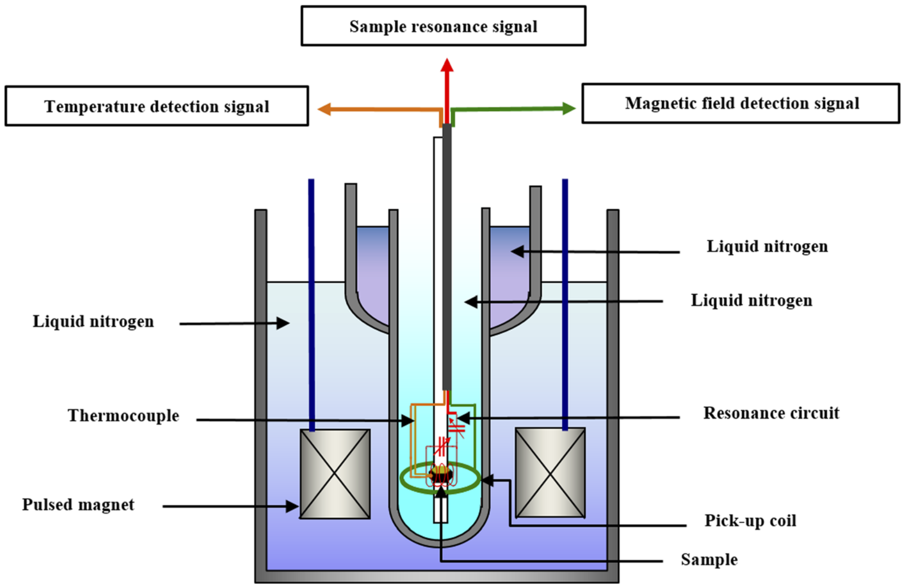

FIG. 18. NMR detection environment in a pulsed magnetic field.

nitrogen, for some materials that require a high-temperature environment, a high-sensitivity temperature controller must be installed near the probe to ensure the normal operation of the experiment.

The ideal PF-NMR probe should be small and delicate. In terms of mechanical structure, positioning of a samples in the Z direction should be adjustable at the operating end of the sample rod, and a flippable platform should be available for rotation angle experiments and to enable NMR experiments with all crystal axes. By adding a digital feedback loop to control the linear movement and rotation of the sample table, greater positioning accuracy (angular accuracy $<0.1°$[112] and displacement accuracy <1 μm[40]) can be achieved. It is helpful to be able to quickly position the sample in the region with the most uniform magnetic field distribution and thereby overcome the problem of spatial inhomogeneity of the field to a certain extent. To overcome the problem of low magnetic field repeatability, an electrical circuit with flexible tuning and a matching coil is placed around the sample, and the circuit is tuned by the feedback control system to achieve resonance conditions and obtain a higher quality factor Q. Meanwhile, impedance matching is imposed to suppress reflected waves. For this part of the system, it is important to have mutual shielding and heat insulation between circuit elements and wires. A pick-up coil should be wound around the sample to measure the electromotive force induced by the magnetic field and thereby monitor the time-dependent intensity. For experiments with temperature changes, a thermocouple auto-verification system is also needed.

The instantaneous release of the pulsed high current will cause strong mechanical vibrations. The LC resonant circuit needs to be fixed on a replaceable board to provide mechanical stability for the circuit while also facilitating sample packaging. At the same time, all the connecting terminals between the probe and the control system and the opening of the movable rod should be sealed to prevent leakage of helium gas.

Generally speaking, the mechanical structure of the NMR probe depends on the geometry of the pulsed magnet aperture, and the resonance parameters depend on the working frequency band of the NMR spectrometer. Installation of samples and adjustment of probes are usually the last critical steps in the preparation of an NMR experiment. At present, RF microcoils are widely used, owing to their good integration capability, inherent sensitivity, high excitation/resonance frequency, and wide receiving bandwidth compared with earlier types.[113,114] However, because of the limited number of laboratories that have the facilities to study matter in extreme pulsed high magnetic fields, such NMR probes have not been extensively studied in the ultrahigh-frequency range. Therefore, the design of appropriate probes with good mechanical and electrical properties is one of the key tasks in the further development of PF-NMR.

V. PERSPECTIVES AND FUTURE DIRECTIONS

As evidenced here, PF-NMR is expected to open up a new perspective for high-field physical property measurement. Especially in the life sciences and condensed matter physics, high magnetic fields are helpful for manipulating and studying the nuclear spin and electronic state properties of strongly correlated electronic materials, thereby providing more information on the complex behavior of these challenging systems. The development of the PF-NMR technique over the past 20 years shows that it is feasible to carry out NMR experiments in pulsed high magnetic fields. However, there are a number of issues that remain.

(1) The advantages of NMR at high magnetic field strength should be stressed within the scientific community. In steady low-field NMR, in order to improve the SNR and optimize signal processing, various methods have already been proposed, and it is not difficult to obtain the same resolution as at high fields. Therefore, it is necessary to understand that the main motivation for developing high-field NMR is to establish ways to observe systems in which special field-induced

effects occur, which represents the principal advantage of PF-NMR. Taking into account the large fluctuations of the unsteady pulsed field, under the premise of not sacrificing the strength of the magnetic field, it is necessary to optimize the magnet structure and to use a power supply topology and power supply method that provide high stability and ripple-free high-current excitation to generate a homogeneously distributed high-intensity magnetic field within a certain duration. It is necessary to meet not only the criterion of an acceptable NMR relaxation time, but also the acquisition conditions for most nuclear magnetic signals. In addition, the quantum controllability of the high magnetic field must be maintained.

(2) NMR devices that are highly adaptable to pulsed high-magnetic-field environments must be made available. Spectrometer designs should be suitable for high-field and high-frequency NMR experiments, with these tailored spectrometers having good electromagnetic shielding performance and timing coordination with the pulsed magnetic field crest. For the probe, the influence of sample volume and resonant coil volume on RF pulse width must be considered, as well as pulse field probe tuning and impedance matching. A comprehensive structural optimization scheme should be developed to allow temperature control, monitoring, and precise positioning of samples. Moreover, the time dependence and repetition error of the magnetic field cannot be ignored. An RF communication loop with high-speed broadband, large-capacity signal transmission and acquisition should be set up. The use of appropriate optimization algorithms and control system strategies should solve the problems of NMR signal phase error and baseline distortion.

(3) The feasibility of observing four key parameters of nuclear magnetic phenomena in the extreme environment of pulsed fields should be explored: Knight/chemical shift, nuclear quadrupole shift, longitudinal relaxation time T_1, and transverse relaxation time T_2. For the first two, improvements in the SNR should be taken as the core task, and the holding time of the pulsed magnetic field should be prolonged to make the nuclear spin as polarized as possible and increase the population difference between different energy levels, thereby giving a high-quality resonance spectrum. With regard to T_1 and T_2, owing to the limited flat-top time that can be achieved with a pulsed magnetic field, it is best to choose a material system with a shorter relaxation time, or to shorten the relaxation time by doping with appropriate reagents. Furthermore, a stable magnetic field can be applied to pre-polarize the nuclear spin to obtain an initial magnetization similar to that in the steady state.

VI. CONCLUSIONS

PF-NMR has both the measurement sensitivity of conventional NMR and the quantum controllability of a high magnetic field. It has the potential to become an important NMR technique and to play significant roles in physics, materials science, chemistry, biomedicine, and other disciplines. Typical applications include but are not limited to the following: (1) It can effectively shorten the NMR detection time of bio-macromolecules, improve the detection sensitivity, and provide a high SNR, high-resolution, and high-throughput detection method, allowing structural determination and the study of dynamic changes of macromolecules such as proteins and nucleic acids. (2) Using the time-varying characteristics of the magnetic field strength at the rising and falling edges of each pulse of the pulsed magnetic field, it is possible to rapidly analyze the nuclear relaxation characteristics of bio-macromolecules and other key nuclear magnetic parameters under different magnetic field intensities, thus significantly improving the sensitivity of nuclear magnetic detection such that the lower limit of detection of sample concentration approaches or even reaches the single-molecule level. (3) The Knight shift and electric field gradient changes can be measured in differently doped samples of high-temperature superconductors, the evolution of spin/charge-ordered states can be explored, it can be determined whether a quantum critical point really exists, and the mechanism(s) of high-temperature superconductivity can be revealed. (4) In strongly correlated systems such as heavy fermion materials and quantum spin liquids, various quantum phase transitions can be observed in an ultrahigh magnetic field. NMR can then be used to measure the line splitting, longitudinal relaxation rate, and transverse relaxation rate caused by magnetic interaction. It is also possible to study the order parameters and fluctuations of various quantum states and to explore the general laws of quantum phase transitions. Other mechanisms affected by magnetic fields, such as structural phase transitions, nematic phase transitions, hidden states, magnetic phase transitions, and re-entrant superconductivity, could also be investigated by NMR methods under extremely high magnetic fields.

PF-NMR has been around for nearly two decades. Owing to technical bottlenecks such as poor magnetic field stability and the low quality of FID signal spectral analysis under such harsh conditions, research has lingered at the exploratory stage. However, once the technical problems of PF-NMR have been overcome and its detection accuracy and reliability are comparable to those of NMR in a steady field, this method should provide an important route to significant discoveries about the properties of matter under extreme conditions in condensed matter physics, materials science, chemistry, biomedicine, and other fields.

Particularly important future avenues of research concern improvements in pulsed magnet technology, spectrometer upgrades, and probe structure optimization. Such efforts are expected to increase the efficiency and widen the range of application of NMR under high fields. Although this work is far from complete, and steady-field NMR will remain the mainstream for some time, PF-NMR still has the prospect of providing a powerful detection method for new phenomena in advanced research.

ACKNOWLEDGMENTS

We would like to thank Professor Chun Tang (Peking University) for help with this manuscript. This work was supported by the National Key Research and Development Program of China (Grany No. 2016YFA0401703) and the National Natural Science Foundation of China (Grany No. 51821005).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

REFERENCES

[1] Z. Gan, P. Gor'kov, A. S. T. Cross, and D. Massiot, "Seeking higher resolution and sensitivity for NMR of quadrupolar nuclei at ultrahigh magnetic fields," J. Am. Chem. Soc. **124**, 5634 (2002).

[2]F.-J. Wu, L. S. Simeral, A. A. Mrse, J. L. Eilertsen, L. Negureanu, Z. Gan, F. R. Fronczek, R. W. Hall, and L. G. Butler, "Structural characterization of $Al_{10}O_6^iBu_{16}(\mu\text{-}H)_2$, a high aluminum content cluster: Further studies of methylaluminoxane (MAO) and related aluminum complexes," Inorg. Chem. **46**, 44 (2007).
[3]Q. Wang, W. Li, I. Hung, F. Mentink-Vigier, X. Wang, G. Qi, X. Wang, Z. Gan, J. Xu, and F. Deng, "Mapping the oxygen structure of γ-Al_2O_3 by high-field solid-state NMR spectroscopy," Nat. Commun. **11**, 3620 (2020).
[4]H. W. Spiess, "NMR spectroscopy: Pushing the limits of sensitivity," Angew. Chem., Int. Ed. **47**, 639 (2008).
[5]J. Liu, Q. Wang, L. Qin, K. Wang, H. Liu, L. Wang, Y. Wang, and Y. D. B. Zhou, "Generation of 32.35 T with an all-superconducting magnet at IEECAS," in *IEEE CSC and ESAS Superconductivity News Forum*, Global ed. (IEEE, 2020).
[6]J. R. Miller, "The NHMFL 45-T hybrid magnet system: Past, present, and future," IEEE Trans. Appl. Supercond. **13**, 1385 (2003).
[7]W. G. Moulton and A. P. Reyes, "Nuclear magnetic resonance in solids at very high magnetic fields," High Magn. Fields **3**, 185 (2006).
[8]Y. Li, A. M. Wolters, P. V. Malawey, J. V. Sweedler, and A. G. Webb, "Multiple solenoidal microcoil probes for high-sensitivity, high-throughput nuclear magnetic resonance spectroscopy," Anal. Chem. **71**, 4815 (1999).
[9]D. Högemann, V. Ntziachristos, L. Josephson, and R. Weissleder, "High throughput magnetic resonance imaging for evaluating targeted nanoparticle probes," Bioconjugate Chem. **13**, 116 (2002).
[10]M. A. Macnaughtan, T. Hou, J. Xu, and D. Raftery, "High-throughput nuclear magnetic resonance analysis using a multiple coil flow probe," Anal. Chem. **75**, 5116 (2003).
[11]R. Freeman and E. Kupče, "New methods for fast multidimensional NMR," J. Biomol. NMR **27**, 101 (2003).
[12]H. Wang, L. Ciobanu, and A. Webb, "Reduced data acquisition time in multidimensional NMR spectroscopy using multiple-coil probes," J. Magn. Reson. **173**, 134 (2005).
[13]J. A. Norcross, C. T. Milling, D. L. Olson, D. Xu, A. Audrieth, R. Albrecht, K. Ruan, J. Likos, C. Jones, and T. L. Peck, "Multiplexed NMR: An automated CapNMR dual-sample probe," Anal. Chem. **82**, 7227 (2010).
[14]M. R. Geller, *Fundamentals of Physics* (Eolss Publishers Co. Ltd., Oxford, UK, 2013).
[15]T. Goto, M. Mori, K. Chiba, T. Suzuki, and T. Fukase, "High-field Cu/La-NMR study on high-T_c cuprate $La_{2-x}Ba_xCuO_4$ ($x = 0.125$)," Physica B **284-288**, 657 (2000).
[16]P. M. C. Rourke, I. Mouzopoulou, X. Xu, C. Panagopoulos, Y. Wang, B. Vignolle, C. Proust, E. V. Kurganova, U. Zeitler, Y. Tanabe, T. Adachi, Y. Koike, and N. E. Hussey, "Phase-fluctuating superconductivity in overdoped $La_{2-x}Sr_xCuO_4$," Nat. Phys. **7**, 455 (2011).
[17]S. E. Sebastian, N. Harrison, E. Palm, T. P. Murphy, C. H. Mielke, R. Liang, D. A. Bonn, W. N. Hardy, and G. G. Lonzarich, "A multi-component Fermi surface in the vortex state of an underdoped high-T_c superconductor," Nature **454**, 200 (2008).
[18]M. Huang, S. Li, Z. Zhang, X. Xiong, X. Li, and Y. Wu, "Multifunctional high-performance van der Waals heterostructures," Nat. Nanotechnol. **12**, 1148 (2017).
[19]J. G. Analytis, R. D. McDonald, S. C. Riggs, J.-H. Chu, G. S. Boebinger, and I. R. Fisher, "Two-dimensional Dirac fermions in a topological insulator: Transport in the quantum limit," Nat. Phys. **6**, 960 (2010).
[20]C.-L. Zhang, S.-Y. Xu, C. M. Wang, Z. Lin, Z. Z. Du, C. Guo, C.-C. Lee, H. Lu, Y. Feng, S.-M. Huang, G. Chang, C.-H. Hsu, H. Liu, H. Lin, L. Li, C. Zhang, J. Zhang, X.-C. Xie, T. Neupert, M. Z. Hasan, H.-Z. Lu, J. Wang, and S. Jia, "Magnetic-tunnelling-induced Weyl node annihilation in TaP," Nat. Phys. **13**, 979 (2017).
[21]T. Caldwell, P. L. Kuhns, W. G. Moulton, A. P. Reyes, P. N. Rogers, and R. N. Shelton, "High field NMR studies of NaV_2O_5 to 44.7 T," Int. J. Mod. Phys. B **16**, 3298 (2008).
[22]M. H. Levitt, *Spin Dynamics: Basics of Nuclear Magnetic Resonance* (John Wiley & Sons, Ltd., Chichester, 2002).
[23]T. Wu, H. Mayaffre, S. Krämer, M. Horvatić, C. Berthier, W. N. Hardy, R. Liang, D. A. Bonn, and M.-H. Julien, "Magnetic-field-induced charge-stripe order in the high-temperature superconductor $YBa_2Cu_3O_y$," Nature **477**, 191 (2011).
[24]D. Shaw, *Fourier Transform NMR Spectroscopy*, 2nd ed, (Elsevier Press; IGE Medical Systems Ltd., Amsterdam; Slough, UK, 1984).
[25]Y.-Y. Lin, S. Ahn, N. Murali, W. Brey, C. R. Bowers, and W. S. Warren, "High-resolution, >1 GHz NMR in unstable magnetic fields," Phys. Rev. Lett. **85**, 3732 (2000).
[26]Z. Gan, H.-T. Kwak, M. Bird, T. Cross, P. Gor'kov, W. Brey, and K. Shetty, "High-field NMR using resistive and hybrid magnets," J. Magn. Reson. **191**, 135 (2008).
[27]M. Li, J. L. Schiano, J. E. Samra, K. K. Shetty, and W. W. Brey, "Reduction of magnetic field fluctuations in powered magnets for NMR using inductive measurements and sampled-data feedback control," J. Magn. Reson. **212**, 254 (2011).
[28]P. J. M. van Bentum, J. C. Maan, J. W. M. van Os, and A. P. M. Kentgens, "Strategies for solid-state NMR in high-field Bitter and hybrid magnets," Chem. Phys. Lett. **376**, 338 (2003).
[29]K. Hashi, T. Shimizu, A. Goto, T. Kiyoshi, S. Matsumoto, H. Wada, T. Fujito, K. Hasegawa, M. Yoshikawa, T. Miki, S. Ito, M. Hamada, and S. Hayashi, "Achievement of a 920-MHz high resolution NMR," J. Magn. Reson. **156**, 318 (2002).
[30]J. Haase, D. Eckert, H. Siegel, H. Eschrig, K. H. Müller, and F. Steglich, "High-field NMR in pulsed magnets," Solid State Nucl. Magn. Reson. **23**, 263 (2003).
[31]J. Haase, D. Eckert, H. Siegel, H. Eschrig, K.-H. Müller, and F. Steglich, "Nuclear magnetic resonance in pulsed high-field magnets," Concepts Magn. Reson., Part B **19**, 9 (2003).
[32]J. Haase, D. Eckert, H. Siegel, K.-H. Müller, H. Eschrig, A. Simon, and F. Steglich, "NMR in pulsed high magnetic fields," J. Magn. Magn. Mater. **272-276**, e1623–e1625 (2004).
[33]J. Haase, "First ^{2}H NMR at 58 T," Appl. Magn. Reson. **27**, 297 (2004).
[34]J. Haase, D. Eckert, H. Siegel, H. Eschrig, K.-H. Müller, A. Simon, and F. Steglich, "NMR at the Frontier of pulsed high field magnets," Physica B **346-347**, 514 (2004).
[35]J. Haase, M. Kozlov, K.-H. Müller, H. Siegel, B. Büchner, H. Eschrig, and A. G. Webb, "NMR in pulsed high magnetic fields at 1.3 GHz," J. Magn. Magn. Mater. **290-291**, 438 (2005).
[36]J. Haase, M. B. Kozlov, A. G. Webb, B. Büchner, H. Eschrig, K.-H. Müller, and H. Siegel, "2 GHz ^{1}H NMR in pulsed magnets," Solid State Nucl. Magn. Reson **27**, 206–208 (2005).
[37]M. B. Kozlov, J. Haase, C. Baumann, and A. G. Webb, "56 T ^{1}H NMR at 2.4 GHz in a pulsed high-field magnet," Solid State Nucl. Magn. Reson. **28**, 64 (2005).
[38]G. Zheng, K. Katayama, M. Nishiyama, S. Kawasaki, N. Nishihagi, S. Kimura, M. Hagiwara, and K. Kindo, "Spin–echo NMR in pulsed high magnetic fields up to 48 T," J. Phys. Soc. Jpn. **78**, 095001 (2009).
[39]S. Kawasaki, T. Motohashi, K. Shimada, T. Ono, R. Kanno, M. Karppinen, H. Yamauchi, and G. Zheng, "Measurement of electron correlations in Li_xCoO_2 ($x = 0.0$–0.35) using ^{59}Co nuclear magnetic resonance and nuclear quadrupole resonance techniques," Phys. Rev. B **79**, 220514 (2009).
[40]B. Meier, J. Kohlrautz, J. Haase, M. Braun, F. Wolff-Fabris, E. Kampert, T. Herrmannsdörfer, and J. Wosnitza, "Nuclear magnetic resonance apparatus for pulsed high magnetic fields," Rev. Sci. Instrum. **83**, 083113 (2012).
[41]G.-Q. Zheng, K. Katayama, M. Kandatsu, N. Nishihagi, S. Kimura, M. Hagiwara, and K. Kindo, "^{59}Co NMR at pulsed high magnetic fields," J. Low Temp. Phys. **159**, 280 (2010).
[42]E. Abou-Hamad, P. Bontemps, and G. L. J. A. Rikken, "NMR in pulsed magnetic field," Solid State Nucl. Magn. Reson. **40**, 42 (2011).
[43]H. Stork, P. Bontemps, and G. L. J. A. Rikken, "NMR in pulsed high-field magnets and application to high-T_C superconductors," J. Magn. Reson. **234**, 30 (2013).
[44]J. Wosnitza, A. D. Bianchi, J. Freudenberger, J. Haase, T. Herrmannsdörfer, N. Kozlova, L. Schultz, Y. Skourski, S. Zherlitsyn, and S. A. Zvyagin, "Dresden pulsed magnetic field facility," J. Magn. Magn. Mater. **310**, 2728 (2007).
[45]F. Weickert, B. Meier, S. Zherlitsyn, T. Herrmannsdörfer, R. Daou, M. Nicklas, J. Haase, F. Steglich, and J. Wosnitza, "Implementation of specific-heat and NMR experiments in the 1500 ms long-pulse magnet at the Hochfeld–Magnetlabor Dresden," Meas. Sci. Technol. **23**, 105001 (2012).
[46]A. Orlova, P. Frings, M. Suleiman, and G. L. J. A. Rikken, "New high homogeneity 55 T pulsed magnet for high field NMR," J. Magn. Reson. **268**, 82 (2016).
[47]E. Dalgaard, E. Auken, and J. J. Larsen, "Adaptive noise cancelling of multichannel magnetic resonance sounding signals," Geophys. J. Int. **191**, 88 (2012).
[48]W. Chen, H. Ma, D. Yu, and H. Zhang, "SVD-based technique for interference cancellation and noise reduction in NMR measurement of time-dependent magnetic fields," Sensors **16**, 323 (2016).

[49]T. Iijima, K. Takegoshi, K. Hashi, T. Fujito, and T. Shimizu, "High-resolution NMR with resistive and hybrid magnets: Deconvolution using a field-fluctuation signal," J. Magn. Reson. **184**, 258 (2007).

[50]T. Iijima and K. Takegoshi, "Compensation of effect of field instability by reference deconvolution with phase reconstruction," J. Magn. Reson. Imaging **191**, 128 (2008).

[51]B. Meier, S. Greiser, J. Haase, T. Herrmannsdörfer, F. Wolff-Fabris, and J. Wosnitza, "NMR signal averaging in 62 T pulsed fields," J. Magn. Reson. **210**, 1 (2011).

[52]J. Kohlrautz, S. Reichardt, E. L. Green, H. Kühne, J. Wosnitza, and J. Haase, "NMR shift and relaxation measurements in pulsed high-field magnets up to 58 T," J. Magn. Reson. **263**, 1 (2016).

[53]J. Kohlrautz, J. Haase, E. L. Green, Z. T. Zhang, J. Wosnitza, T. Herrmannsdörfer, H. A. Dabkowska, B. D. Gaulin, R. Stern, and H. Kühne, "Field-stepped broadband NMR in pulsed magnets and application to $SrCu_2(BO_3)_2$ at 54 T," J. Magn. Reson. **271**, 52 (2016).

[54]J. Zeng, P. Zhou, and B. R. Donald, "Protein side-chain resonance assignment and NOE assignment using RDC-defined backbones without TOCSY data," J. Biomol. NMR **50**, 371 (2011).

[55]Q. Xing, P. Huang, J. Yang, J. Sun, Z. Gong, X. Dong, *et al.* "Visualizing an ultra-weak protein–protein interaction in phosphorylation signaling," Angew. Chem., Int. Ed **53**, 11501–11505 (2014).

[56]Z. Liu, Z. Gong, D.-C. Guo, W.-P. Zhang, and C. Tang, "Subtle dynamics of holo glutamine binding protein revealed with a rigid paramagnetic probe," Biochemistry **53**, 1403 (2014).

[57]W.-X. Jiang, X.-H. Gu, X. Dong, and C. Tang, "Lanthanoid tagging via an unnatural amino acid for protein structure characterization," J. Biomol. NMR **67**, 273 (2017).

[58]Z. Gong, X. Gu, D. Guo, J. Wang, and C. Tang, "Protein structural ensembles visualized by solvent paramagnetic relaxation enhancement," Angew. Chem., Int. Ed. **56**, 1002 (2020).

[59]Z. Gong, C. D. Schwieters, and C. Tang, "Theory and practice of using solvent paramagnetic relaxation enhancement to characterize protein conformational dynamics," Methods **148**, 48 (2018).

[60]L. J. Berliner, "The evolution of biomedical EPR (ESR)," Biomed. Spectrosc. Imaging **5**, 5 (2016).

[61]J. J. Inbaraj, T. B. Cardon, M. Laryukhin, S. M. Grosser, and G. A. Lorigan, "Determining the topology of integral membrane peptides using EPR spectroscopy," J. Am. Chem. Soc. **128**, 9549 (2006).

[62]V. F. Mitrovic, E. E. Sigmund, M. Eschrig, H. N. Bachman, W. P. Halperin, A. P. Reyes, P. Kuhns, and W. G. Moulton, "Spatially resolved electronic structure inside and outside the vortex cores of a high-temperature superconductor," Nature **413**, 501 (2006).

[63]H. Zuo, J. Bao, Y. Liu, J. Wang, Z. Jin, Z. Xia, L. Li, Z. Xu, J. Kang, Z. Zhu, and G. Cao, "Temperature and angular dependence of the upper critical field in $K_2Cr_3As_3$," Phys. Rev. B **95**, 014502 (2017).

[64]L. Balicas, J. S. Brooks, K. Storr, S. Uji, M. Tokumoto, H. Tanaka, H. Kobayashi, A. Kobayashi, . V. Barzykin, and L. P. Gor'kov, "Superconductivity in an organic insulator at very high magnetic fields," Phys. Rev. Lett. **87**, 067002 (2001).

[65]S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, and H. Kobayashi, "Magnetic-field-induced superconductivity in a two-dimensional organic conductor," Nature **410**, 908 (2001).

[66]K. Ishida, H. Mukuda, Y. Kitaoka, K. Asayama, Z. Q. Mao, Y. Mori, and Y. Maeno, "Spin-triplet superconductivity in Sr_2RuO_4 identified by ^{17}O Knight shift," Nature **396**, 658 (1998).

[67]A. Pustogow, Y. Luo, A. Chronister, Y.-S. Su, D. A. Sokolov, F. Jerzembeck, A. P. Mackenzie, C. W. Hicks, N. Kikugawa, S. Raghu, E. D. Bauer, and S. E. Brown, "Constraints on the superconducting order parameter in Sr_2RuO_4 from oxygen-17 nuclear magnetic resonance," Nature **574**, 72 (2019).

[68]K. Matano, M. Kriener, K. Segawa, Y. Ando, and G. Zheng, "Spin-rotation symmetry breaking in the superconducting state of $Cu_xBi_2Se_3$," Nat. Phys. **12**, 852 (2016).

[69]P. Fulde and R. A. Ferrell, "Superconductivity in a strong spin-exchange field," Phys. Rev. **135**, A550 (1964).

[70]A. I. Larkin and Y. N. Ovchinnikov, "Density of states in inhomogeneous superconductors," Sov. Phys. JETP **34**, 1144 (1972).

[71]Y. Matsuda and H. Shimahara, "Fulde–Ferrell–Larkin–Ovchinnikov state in heavy fermion superconductors," J. Phys. Soc. Jpn. **76**, 051005 (2007).

[72]J. Wright, E. Green, P. Kuhns, A. Reyes, J. Brooks, J. Schlueter, R. Kato, H. Yamamoto, M. Kobayashi, and S. Brown, "Zeeman–driven phase transition within the superconducting state of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$," Phys. Rev. Lett. **107**, 087002 (2011).

[73]H. Mayaffre, S. Krämer, M. Horvatić, C. Berthier, K. Miyagawa, K. Kanoda, and V. F. Mitrović, "Evidence of Andreev bound states as a hallmark of the FFLO phase in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$," Nat. Phys. **10**, 928 (2014).

[74]G. Koutroulakis, H. Kühne, J. A. Schlueter, J. Wosnitza, and S. E. Brown, "Microscopic study of the Fulde–Ferrell–Larkin–Ovchinnikov state in an all-organic superconductor," Phys. Rev. Lett. **116**, 067003 (2016).

[75]Y. Wang, X. Zhang, F. Pollmann, M. Cheng, and Z. Y. Meng, "Quantum spin liquid with even ising gauge field structure on Kagome lattice," Phys. Rev. Lett. **121**, 057202 (2018).

[76]N. Ma, G. Sun, Y. You, C. Xu, A. Vishwanath, A. W. Sandvik, and Z. Y. Meng, "Dynamical signature of fractionalization at the deconfined quantum critical point," Phys. Rev. B **98**, 174421 (2018).

[77]B. Zhao, P. Weinberg, and A. W. Sandvik, "Symmetry-enhanced discontinuous phase transition in a two-dimensional quantum magnet," Nat. Phys. **15**, 678 (2019).

[78]F. Weickert, A. A. Aczel, M. B. Stone, V. O. Garlea, C. Dong, Y. Kohama, R. Movshovich, A. Demuer, N. Harrison, M. B. Gamża, A. Steppke, M. Brando, H. Rosner, and A. A. Tsirlin, "Field-induced double dome and Bose–Einstein condensation in the crossing quantum spin chain system $AgVOAsO_4$," Phys. Rev. B **100**, 104422 (2019).

[79]K. Purcell, D. Graf, M. Kano, J. Bourg, E. Palm, T. Murphy, R. McDonald, C. Mielke, M. M. Altarawneh, C. Petrovic, R. Hu, T. Ebihara, J. Cooley, P. Schlottmann, and S. W. Tozer, "Pressure evolution of a field induced Fermi surface reconstruction and of the Neel critical field in $CeIn_3$," Phys. Rev. B **79**, 214428 (2009).

[80]Y. Tokunaga, A. Orlova, N. Bruyant, D. Aoki, H. Mayaffre, S. Krämer, M. H. Julien, C. Berthier, M. Horvatić, N. Higa, T. Hattori, H. Sakai, S. Kambe, and I. Sheikin, "High-field phase diagram of the heavy-fermion metal $CeIn_3$: Pulsed-field NMR study on single crystals up to 56 T," Phys. Rev. B **99**, 085142 (2019).

[81]K. Kodama, M. Takigawa, M. Horvatić, C. Berthier, H. Kageyama, Y. Ueda, S. Miyahara, F. Becca, and F. Mila, "Magnetic superstructure in the two-dimensional quantum antiferromagnet $SrCu_2(BO_3)_2$," Science **298**, 395 (2002).

[82]M. Takigawa, M. Horvatić, T. Waki, S. Krämer, C. Berthier, F. Lévy-Bertrand, I. Sheikin, H. K. Y. Ueda, and F. Mila, "Incomplete Devil's staircase in the magnetization curve of $SrCu_2(BO_3)_2$," Phys. Rev. Lett. **110**, 067210 (2013).

[83]M. Takigawa, S. Matsubara, M. Horvatić, C. Berthier, H. Kageyama, and Y. Ueda, "NMR evidence for the persistence of a spin superlattice beyond the 1/8 magnetization plateau in $SrCu_2(BO_3)_2$," Phys. Rev. Lett. **101**, 037202 (2008).

[84]R. Stern, I. Heinmaa, P. Kuhns, A. Reyes, W. Moulton, H. Dabkowska, and B. Gaulin, "High field 11B NMR study of 1/3 magnetization plateau of 2D quantum spin system $SrCu_2(BO_3)_2$," National High Magnetic Field Laboratory, Research Report (2004), https://www.academia.edu/17987882/HIGH_FIELD_11B_NMR_STUDY_OF_1_3_MAGNETIZATION_PLATEAU_OF_2D_QUANTUM_SPIN_SYSTEM_SrCu2_BO3_2.

[85]M. Jaime, R. Daou, S. A. Crooker, F. Weickert, A. Uchida, A. E. Feiguin, C. D. Batista, H. A. Dabkowska, and B. D. Gaulin, "Magnetostriction and magnetic texture to 100.75 Tesla in frustrated $SrCu_2(BO_3)_2$," Proc. Natl. Acad. Sci. U. S. A. **109**, 012404 (2012).

[86]Y. H. Matsuda, N. Abe, S. Takeyama, H. Kageyama, P. Corboz, A. Honecker, S. R. Manmana, G. R. Foltin, K. P. Schmidt, and F. Mila, "Magnetization of $SrCu_2(BO_3)_2$ in ultrahigh magnetic fields up to 118 T," Phys. Rev. Lett. **111**, 137204 (2013).

[87]K. Nawa, M. Takigawa, M. Yoshida, and K. Yoshimura, "Anisotropic spin fluctuations in the quasi one-dimensional frustrated magnet $LiCuVO_4$," J. Phys. Soc. Jpn. **82**, 094709 (2013).

[88]N. Büttgen, K. Nawa, T. Fujita, M. Hagiwara, P. Kuhns, A. Prokofiev, A. P. Reyes, L. E. Svistov, K. Yoshimura, and M. Takigawa, "Search for a spin-nematic phase in the quasi-one-dimensional frustrated magnet $LiCuVO_4$," Phys. Rev. B **90**, 134401 (2014).

[89]A. Orlova, E. L. Green, J. M. Law, D. I. Gorbunov, G. Chanda, S. Krämer, M. Horvatić, R. K. Kremer, J. Wosnitza, and G. L. J. A. Rikken, "Nuclear magnetic resonance signature of the spin-nematic phase in $LiCuVO_4$ at high magnetic fields," Phys. Rev. Lett. **118**, 247201 (2017).
[90]Y. Kohama, H. Ishikawa, A. Matsuo, K. Kindo, N. Shannon, and Z. Hiroi, "Possible observation of quantum spin-nematic phase in a frustrated magnet," Proc. Natl. Acad. Sci. U. S. A. **116**, 10686 (2019).
[91]G. L. Kuang and S. F. Shao, "The technologies and scientific researches of steady high magnetic field," Sci. Sin. **44**, 1049 (2014) (in Chinese).
[92]X. Han, T. Peng, H. Ding, T. Ding, Z. Zhu, Z. Xia, J. Wang, J. Han, Z. Ouyang, Z. Wang, Y. Han, H. Xiao, Q. Cao, Y. Lv, Y. Pan, and L. Li, "The pulsed high magnetic field facility and scientific research at Wuhan National High Magnetic Field Center," Matter Radiat. Extremes **2**, 278 (2017).
[93]L. Garrido and N. Beckmann, *New Applications of NMR in Drug Discovery and Development* (Royal Society of Chemistry, Cambridge, 2013).
[94]A. G. Palmer, "NMR characterization of the dynamics of biomacromolecules," Chem. Rev. **104**, 3623 (2004).
[95]R. D. A. Alvares, A. Hasabnis, R. S. Prosser, and P. M. Macdonald, "Quantitative detection of PEGylated biomacromolecules in biological fluids by NMR," Anal. Chem. **88**, 3730 (2016).
[96]M. J. Duer, *Solid State NMR Spectroscopy: Principles and Applications* (Blackwell Science Ltd, Osney Mead, Oxford, 2002).
[97]C. Bonhomme, C. Gervais, and D. Laurencin, "Recent NMR developments applied to organic–inorganic materials," Prog. Nucl. Magn. Reson. Spectrosc. **77**, 1 (2014).
[98]The late Amsterdam 40 T magnet, Universiteit van Amsterdam, https://iop.fnwi.uva.nl/cmp/klaasse/amsterdam40t.html, 1959–2003.
[99]F. Herlach and N. Miura, *High Magnetic Fields: Science and Technology* (World Science Publishing Co. Pte. Ltd., Singapore, 2003).
[100]L. J. Campbell, H. J. Boenig, D. G. Rickel, J. B. Schillig, H. J. Schneider-Muntau, and J. R. Sims, "The NHMFL long-pulse magnet system-60-100 T," Physica B. **216**, 218 (1996).
[101]R. Grössinger, H. Sassik, O. Mayerhofer, E. Wagner, and M. Schrenk, "Austromag: Pulsed magnetic fields beyond 40 T," Physica B. **346-347**, 609 (2004).
[102]H. Ding, J. Hu, W. Liu, Y. Xu, C. Jiang, T. Ding, L. Li, X. Duan, and Y. Pan, "Design of a 135 MW power supply for a 50 T pulsed magnet," IEEE Trans. Appl. Supercond. **22**, 5400504 (2012).
[103]H. Xiao, Y. Ma, Y. Lv, T. Ding, S. Zhang, F. Hu, L. Li, and Y. Pan, "Development of a high-stability flat-top pulsed magnetic field facility," IEEE Trans. Power Electron. **29**, 4532 (2014).
[104]Y. Kohama and K. Kindo, "Generation of flat-top pulsed magnetic felds with feedback control approach," Rev. Sci. Instrum. **86**, 104701 (2015).
[105]S. Zhang, Z. Wang, T. Ding, H. Xiao, J. Xie, and X. Han, "Realization of high-stability flat-top pulsed magnetic fields by a bypass circuit of IGBTs in the active region," IEEE Trans. Power Electron. **35**, 2436 (2020).
[106]F. Jiang, T. Peng, H. Xiao, J. Zhao, Y. Pan, F. Herlach, and L. Li, "Design and test of a flat-top magnetic field system driven by capacitor banks," Rev. Sci. Instrum. **85**, 045106 (2014).
[107]S. Wang, T. Peng, F. Jiang, S. Jiang, S. Chen, L. Deng, R. Huang, and L. Li, "Upgrade of the pulsed magnetic field system with flat-top at the WHMFC," IEEE Trans. Appl. Supercond. **30**, 4900404 (2020).
[108]H. Gao and Z. Zhang, *Nuclear Magnetic Resonance* (Wuhan University Press, Wuchang, 2008) (in Chinese).
[109]M. Motokawa, "Physics in high magnetic fields," Rep. Prog. Phys. **67**, 1995 (2004).
[110]J. Haase, S. K. Goh, T. Meissner, P. L. Alireza, and D. Rybicki, "High sensitivity nuclear magnetic resonance probe for anvil cell pressure experiments," Rev. Sci. Instrum. **80**, 073905 (2009).
[111]T. Kissikov, R. Sarkar, B. T. Bush, M. Lawson, P. C. Canfield, and N. J. Curro, "Nuclear magnetic resonance probe head design for precision strain control," Rev. Sci. Instrum. **88**, 103902 (2017).
[112]Q.-Y. Liu, J.-F. Wang, H.-K. Zuo, M. Yang, and X.-T. Han, "Electrical transport measurement system in pulsed high magnetic field based on rotation sample rod," Acta Phys. Sin. **68**, 230701 (2019) (in Chinese).
[113]H. Janssen, A. Brinkmann, E. R. H. van Eck, P. J. M. van Bentum, and A. P. M. Kentgens, "Microcoil high-resolution magic angle spinning NMR spectroscopy," J. Am. Chem. Soc. **128**, 8722 (2006).
[114]A. G. Webb, "Radiofrequency microcoils for magnetic resonance imaging and spectroscopy," J. Magn. Reson. **229**, 55 (2013).