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Design of a permanent magnet with a mechanical sweep suitable for variable-temperature continuous-wave and pulsed EPR spectroscopy

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ABSTRACT

A magnetic system is introduced which consists of three nested rings of permanent magnets of a Halbach dipolar layout and is capable for EPR spectroscopy. Two of the rings can be rotated independently to adjust the magnetic flux in the center and even allow for mechanical field sweeps. The presented prototype achieves a magnetic flux range of 0.0282–0.3013 T with a minimal sweep of 0.15 mT and homogeneity of about 10^{-3}.

First applications with CW and pulsed Mims ENDOR as well as ESEEM experiments on a sample of a glycine single crystal doped with 1% copper nitrate demonstrate that flux range, sweep accuracy and homogeneity of this prototype is sufficient for EPR experiments on most solid samples.

Together with a recently improved design magnets can be build which could serve as compact and easily transportable replacement of standard electromagnets with negligible consumption of power or coolants.

1. Introduction

Since the advent of commercial spectrometers at the end of the 1980s pulsed electron paramagnetic resonance (EPR) spectroscopy [1] has spread from a small community of method developing groups to a significant fraction of the groups that are mainly concerned with EPR applications in physics, chemistry, and biology. The recent surge of distance measurements in the nanometer range by pulsed EPR [2,3] on spin-labeled biomacromolecules [4,5] indicates a great potential for further widening of the application of pulsed EPR in structural biology. Continuous-wave (CW) EPR spectrometers at X-band frequencies of about 9.6 GHz can be built with small electromagnets that may not even need water cooling or with permanent magnets [6–13]. However, the existing designs are not well suited for a pulsed EPR spectrometer. First, the gap of the magnet is too small to accommodate a pulsed EPR probehead inside a cryostat, as is necessary since most pulsed EPR experiments have to be performed with liquid nitrogen or liquid helium cooling. Second, while the major contribution to the magnetic field is supplied by the permanent magnet, adjustment of the electron spin resonance frequency to the fixed microwave frequency of the spectrometer is achieved by an additional sweep coil which continuously consumes electrical power. This is not a disadvantage for CW EPR experiments where the field is swept during the whole measurement process, but causes unnecessary power consumption in the majority of pulsed EPR experiments that are performed at fixed field and frequency. Additionally, such coils require extra space and generate heat, which might change the temperature of the permanent magnets and hence the resulting field. On the other hand, sweep capability for the magnetic field is required to record the EPR spectrum of the sample before setup of the pulse experiment and to adjust the resonance field to the desired position in the spectrum.

Here we present the design of a permanent magnet with a resulting magnetic field which can be mechanically swept and can be operated at a fixed field without power consumption at any point within its sweep range. Furthermore, it is big enough to accommodate a standard flow cryostat and probe head as used in current commercial X-band pulse EPR spectrometers. The complete magnet consists of three nested Halbach Mandhala magnet rings that can be rotated with respect to each other by two stepper motors and has a flux range from 0.0282 to 0.3013 T. The field homogeneity is sufficient for EPR applications as is demonstrated by CW EPR, electron spin echo envelope modulation (ESEEM) and pulsed electron nuclear double resonance (ENDOR) experiments on Cu(II) doped into a crystal of glycine. The magnet has a size of 840 × 440 × 340 mm and weighs 47 kg. The size for instrumentation (probeheads and cryostats) is limited by the inner diameter of 80 mm.

Recently this design has been improved to generate 0.2–0.45 T with a homogeneity of better than 400 Hz (i.e. ca. 50–20 ppm) over

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5 mm DSV (diameter of a spherical volume). This magnet consists only of two nested Halbach rings and weights about 30 kg. However, it was not equipped with a mechanical sweep [14].

2. Materials and methods

2.1. Sample preparation

A concentrated solution of glycine (Aldrich) in deionized Milli-Q water was doped with 1 Mol% copper(II)nitrate (Aldrich). Slow evaporation of the water at ambient temperature provided pale blue crystals of a convenient size for measurements in a standard EPR tube (Wilmad).

2.2. EPR measurements

All EPR measurements were performed with a Bruker Elexsys 580 spectrometer at a temperature of 15 K, using helium cooling with a flow cryostat (Oxford instruments). The whole flow cryostat (outer diameter of 70 mm), which doubles as a probe holder in the Bruker spectrometer, was placed inside the bore of the home-built magnet. Because the field generated by permanent magnets is temperature dependent (here a drift of about a tenth of a sweep step was observed over temperature drifts of about 3 °C, see also Table 1), the measurements were conducted in an air-conditioned lab at $T = 23 \pm 0.5$ °C (measured over a duration of 10 h). The probehead was connected to the microwave bridge of the spectrometer by a flexible coaxial microwave cable of 1.5 m length. CW EPR at a frequency of 9.768105 GHz was performed with a power of 20 μW (40 dB attenuation) and a modulation amplitude of 0.2 mT. The sweep acquisition of the spectrometer was externally triggered by a TTL signal derived from a contact switch at the magnet. The actual sweep width of 10 mT was set by adjusting the sweep times of the home-built magnet and of the spectrometer. No further synchronization during the sweep was applied. The CW EPR spectrum is the sum of ten scans.

Mims ENDOR was performed with a repetition time of 1.024 ms and pulse lengths of 28 ns for the microwave $\pi/2$ pulses and 14 μs for the radiofrequency pulse. A $[(+x)-(-x)]$ phase cycle was performed on the first $\pi/2$ pulse to obtain zero baseline. The spectrum is the sum of 9 scans with two times 100 shots per scan corresponding to a total measurement time of 60 min. Three-pulse ESEEM was performed with a repetition time of 2.048 ms and pulse lengths of 28 ns for the $\pi/2$ pulses and a $[(+x,+x)-(-x,+x)-(+x,-x)+(-x,-x)]$ phase cycle on the first and last pulse to cancel echo crossings. The delay between the first two pulses (rising flank to rising flank) was 200 ns and the initial delay between the second and third pulse was 320 ns. The time trace consists of 2048 data points with an increment of 16 ns. The time trace is the sum of 5 scans with four times 30 shots per scan corresponding to a total measurement time of 42 min.

Table 1
Summary of the technical data.

Physical dimensions	Number	Length (mm)	Width (mm)	Height (mm)
Magnet system	1	800	400	500
Magnet blocks	576	13	13	17
Weight/Diameterss		**Weight (kg)**		**Inner bore (mm)**
Magnet		75		81
Controller		15		
Field range		**Minimum**	**Maximum**	**Min. step**
Magnet [G]		282	3014	1.5
Temperature drift [G/K]			−0.05	
Homogeneity		See Fig. 3		

3. Results and discussion

3.1. Concept of the permanent magnet

Two-dimensional magnetization patterns possessing one-sided flux were first proposed theoretically in 1973 by Mallinson [15]. These were referred at the time as a "magnetic curiosity", and later realized by Klaus Halbach [16,17], who developed this idea further, and constructed arrangements of permanent multipole magnets, nowadays known as Halbach arrays. They can consist of a different number of individually shaped magnets, depending on the particular layout and purpose of the magnet-arrangement. The optimized construction of dipolar, circular Halbach arrays from identical magnets was described by Raich and Blümler [13]. The advantage of using identical rather than individually shaped and magnetized magnets is explained by the strong variation (up to 10%) of the magnetic properties of commercially available materials. In order to construct Halbach arrays with homogeneities better than 10^{-3} the magnets can be arranged in such ways that their deviations compensate- a process which is easier realized with a large number of "identical" magnets. The magnetic field inside the resulting arrays is perpendicular to the principal axis of the cylinder, having mainly planar components. Ideally the magnetic field is completely confined inside the cylinder, hence, making optimal use of the mounted magnetization and achieving high homogeneities (typically $\Delta B/B < 10^{-3}$).

3.2. Magnet design

The properties described above allow for characterizing the resulting magnetic flux inside a Halbach circular dipole array by a single vector. Consequently such circular arrays can be concentrically nested one inside the other with the possibility to perform mechanical rotations with only small torque relative to each other by angular displacement θ [18]. As a result the total magnetic field at its center varies as a function of this angle [14,18–20]. When non-linearities in the magnetic hysteresis loop can be ignored (as it is the case with the magnetically very hard rare-earth alloys), the total magnetic field is the vectorial sum of the magnetic fields from all nested arrays. If two Halbach circular arrays are designed in such a way that their magnetic fluxes have the same magnitude B, it is in principle possible to vary the total magnetic flux from zero, when the vectors are antiparallel ($\theta = 180°$), up to $2B$ for parallel flux vectors ($\theta = 0°$). In reality however, imperfections in construction, dimensional tolerances and homogeneity of the permanent magnets limit these ideal values.

The objective of this work was to devise a magnet arrangement which allows a coarse adjustment of the magnetic field to the desired EPR resonance by two rings while a third ring with a weaker field allows a mechanical field sweep around this value.

The inner ring is fixed and its flux vector (B_i) defines the z-direction. The middle ring and hence its flux vector (B_m) is rotated relative to z by an angle θ while the outer ring (B_o) is at an angle φ relative to z. The resulting magnetic flux, B_e, is then the vector sum of all three vectors and amounts to

$$B_e = \sqrt{B_i^2 + B_m^2 + B_o^2 + 2B_i(B_m\cos\theta + B_o\cos\varphi) + 2B_mB_o(\sin\theta\sin\varphi + \cos\theta\cos\varphi)} \quad (1)$$

Following the concept of NMR-Mandhalas [13] all three rings were designed to be assembled from identical magnet blocks (dimensions 17 × 17 × 14 mm) of FeNdB (maximum energy product about 45 MGOe and a remanence of $B_r \approx 1.35$ T, produced by Ningbo, Ningang, Peoples Republic of China). This design (see Fig. 1) results in the following values: the inner ring with 16 magnets provides 48% of the total maximal field or $B_i = 145$ mT, the middle ring 30%